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SUCCINIMID.

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PART I.

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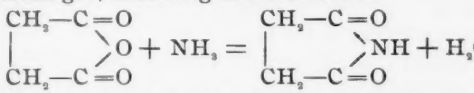
SUCCINIMID was discovered in the year 1835 by Felix d' Arcet,[1] who prepared it by acting on succinic anhydride with ammonia gas, according to the reaction.



He noticed that when the two bodies were allowed to react, there was a great elevation of temperature, that a considerable amount of water was evolved, and that a compound much more fusible than succinic acid resulted; by aiding the reaction with heat, a white substance was sublimed which had none of the properties of succinic acid.

D' Arcet found that this substance which he called succinamid, crystallized in regular rhombs from ether and alcohol and contained one molecule of water when crystallized from that solvent, also it gave off ammonia when treated with hot caustic potash. He considered the formula as $C_8H_5NO_2$ from his analysis which would correspond to $C_4H_5NO_2$, according to the atomic weights now in use.

Bisuccinimid. This compound is identical with that prepared by D' Arcet and was so named by Fehling[2] who prepared it by conducting dry ammonia-gas over melted succinic acid, and recrystallizing the sublimate. He announced the melting point to be 210° C. Fehling also prepared this compound by

[1] *Ann. chim. phys.*, [2] 58, 282–300, *1835*.

[2] *Ann. Chem.*, (Liebig), 49, 98, *1844*.

neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and then distilling; ammonia and water go off first and then bisuccinimid and a little succinic acid are sublimed.

$$\begin{array}{l} CH_2-C=O \\ \quad\quad\quad\ \backslash O-NH_4 \\ \quad\quad\quad\ /O-NH_4 \\ CH_2-C=O \end{array} = \begin{array}{l} CH_2-C=O \\ \quad\quad\quad\ \backslash NH \\ \quad\quad\quad\ /\ \ \ \ \ + 2H_2O + NH_3 \\ CH_2-C=O \end{array}$$

Bisuccinimid was also obtained similarly from acid ammonium succinate by the splitting off of water.

Fehling found that an aqueous solution of bisuccinimid dissolved lead oxide in great quantities giving the lead salt containing fifty-eight per cent. of lead. He also announced that barium gave a similar compound.

The name succinimid was given to the compound by Laurent and Gerhardt[1] who devoted considerable time to its investigation, and first prepared the silver salt.

Trisuccinimid was prepared by Gerhardt and Chiozza[2] by the action of succinyl chloride on silver succinimid as follows: $C_2H_4(CO)_2Cl_2 + 2AgN\ (CO)_2\ C_2H_4 = N_2(C_4H_4O_2)_2 + 2AgCl$.

Teuchert,[3] in his experiments on succinamic acid, gives the following statements concerning succinimid:

1. By treating succinimid with barium hydroxide the barium salt of succinamic acid is obtained.

2. On decomposing salts of succinamic acid by acids with the aid of heat, ammonium succinate is formed, not succinimid, as stated by Laurent and Gerhardt.

3. The compound called silver succinamate by Laurent and Gerhardt must not be considered as this compound, but as a silver hydroxide succinimid.

Teuchert also prepared the potassium, magnesium, manganese, cadmium, zinc, and copper salts of succinimid.

In 1869 Erlenmeyer[4] redetermined the melting point of succinimid and found that instead of being 210° as stated by both Fehling and Teuchert, it was 125°–126°. Erlenmeyer denied the

[1] *Compt. rend.*, *1847*, 291, and *1849*, 108.
[2] *Ann. Chem.*, (Liebig), **134**, 136, *1865*.
[3] *Ann. Chem.*, (Liebig), **134**, 136, *1865*.
[4] *Ztschr. fur Chemie*, **12**, 174, *1869*.

conjecture made by Mendelejeff that succinimid might be identical with the isomeric compound, cyanpropionic acid on account of its formation from succinic anhydride, and from succinamid by the decomposition of two NH_2 groups into NH and NH_3: he ascribed its acid properties to the fact that the hydrogen is combined with a nitrogen attached to the rest of the molecule by two CO groups, and further states that it is an imid, and, therefore, plays the part of a monobasic acid.

Bunge,[1] in 1870, confirmed the melting point of succinimid obtained by Erlenmeyer; he found that it crystallized free from water when acetone was used as a solvent and obtained rhombic octahedra, whose axes were as follows: brachydiag.: makrodiag.: vertic. $a : b : c = 0.7888 : 1 : 1.3655$.

Bunge first replaced the hydrogen of the NH group by a nonmetallic element when he formed iodine succinimid by treating silver succinimid with iodine dissolved in acetone or ether. The iodine succinimid reacted with silver nitrate and formed succinimid again. Menshutkin,[2] in 1872, found that there existed two silver compounds with succinimid, one containing no water of crystallization and the other one-half a molecule. He also states that the hydrogen of the NH group can be replaced by mercury, but that the lead, barium or calcium oxides convert it into the corresponding salt of succinamic acid, thus confirming Teuchert's results.

Succinimid may be converted into the amide by alcoholic ammonia at the temperature of the room, or more quickly by heating them together in a sealed tube at 100° C.

Menshutkin prepared succinimid by distilling succinic acid with acetamide. $C_4H_6O_4 + C_2H_3ONH_2 = C_4H_4O_2NH + C_2H_4O_2 + H_2O$.

He also gave the following definition of an imid: "The imid is that acid amide, which, by the taking up of water, gives the amic acid, and by absorption of ammonia gives the amide." To Menshutkin[3] belongs the distinction of first preparing an organic compound of succinimid; he accomplished this by distilling succinic acid and ethylamine and also by their solution in

[1] *Ann. Chem.*, (Liebig), Suppl., **7**, 118, *1870*.
[2] *Ann. Chem.*, (Liebig), **162**, 166, *1872*.
[3] *Ann. Chem.*, (Liebig), **182**, 90, *1876*.

the proper proportions. Ethyl succinimid melts at 26° and boils at 234°, has a vapor density of 4.61 (compared to air) and is easily soluble in water, alcohol or ether. It is entirely decomposed into ethylamine and succinic acid by treating with caustic potash, and by gentle warming with barium hydroxide, gives the characteristic conversion into ethyl succinamic acid. Methyl succinimid, was similarly prepared.

The first evidence of the symmetrical formula of succinimid is found in the statement of Bell[1] that succinimid by distillation with zinc dust, or on reducing its vapor by hydrogen, yields pyrrol; the presence of pyrrol is shown by the reaction with pine moistened with hydrochloric acid.

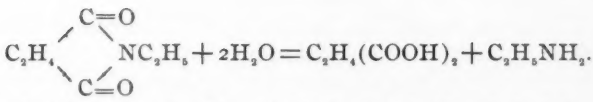
This fact is confirmed by Bernthsen[2] who repeated the experiments, and who also investigated the action of phosphorus trichloride on succinimid, and announced that it gave a fluid chloride. Erlenmeyer's statement that succinimid was not identical with cyanpropionic acid was confirmed in 1882 by Landsberg[3] who, besides preparing a number of metallic salts of succinimid, found that ethyl succinimid when decomposed gave ethylamine and not ethyl alcohol. (This fact was first observed by Menshutkin, but he drew no conclusions from it.) Landsberg made the following statement of the matter:

If succinimid is $C_2H_4\begin{matrix}-CN\\-COOH\end{matrix}$ then the ethyl ester is $C_2H_4\begin{matrix}-CN\\-COOC_2H_5\end{matrix}$; this body by treatment with either bases or acids would give

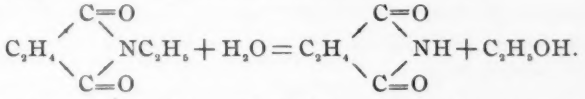
$$\begin{matrix}CH_2-CN\\|\\CH_2COOC_2H_5\end{matrix} + 3H_2O = \begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix} + NH_3 + CH_{25}OH.$$

But if succinimid is $C_2H_4\begin{matrix}C=O\\NH\\C=O\end{matrix}$ the ethyl ester is $C_2H_4\begin{matrix}C=O\\NC_2H_5\\C=O\end{matrix}$ and such a body would give

[1] *Ber. d. chem. Ges.*, **13**, 877, *1880*.
[2] *Ber. d. chem. Ges.*, **13**, 1047, *1880*.
[3] *Ann. Chem.*, (Liebig), **215**, 172, *1882*.

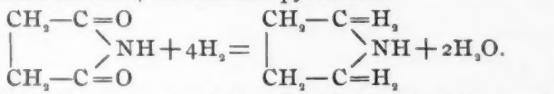


The fact that Menshutkin obtained succinimid and alcohol when he treated silver succinimid with ethyl iodide instead of ethyl succinimid and silver iodide, is explained by the water of crystallization present in some silver succinimid which decomposes the ethyl ester of succinimid first formed as follows:



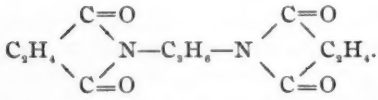
Cimian and Silber[1] investigated the action of bromine on succinimid. They found that the hydrogen of the imid group was not attacked but that when a calculated amount of bromine was dropped into a flask containing succinimid heated to 160° C., that hydrobromic acid was given off, and bibrommaleicimid $(CBr)_2(CO)_2NH$ was formed (M. P. 225° C). This imid when treated with aqueous caustic potash gave bibrommaleic acid. The corresponding anhydride, and the barium and silver results were also made. Bender[2] treated succinimid with calcium chloride in acetic-acid solution and obtained chlorine succinimid $C_2H_4(CO)_2NCl$, which crystallizes in large colorless crystals from boiling benzene, melts at 148° C. without decomposition, and by treatment with hydrochloric acid or alkalies forms succinimid again.

Ladenburg[3] found that by reducing succinimid by sodium, in an alcoholic solution, he obtained pyrrolidin.



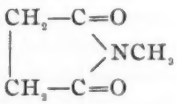
A curious body was made by Strache[4] by heating together two molecules of succinic anhydride and one of propylene diamine, called propylene succinimid. Its melting point is 98°–100° C. and has the formula

[1] *Ber. d. chem. Ges.*, **17**, 556, *1884*.
[2] *Ber. d. chem. Ges.*, **19**, 2273, *1886*.
[3] *Ber. d. chem. Ges.*, **20**, 215, *1887*.
[4] *Ber. d. chem. Ges.*, **21**, 2360, *1888*.

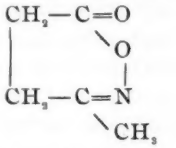


A most extraordinary method of making methyl succinimid was announced by Bredt and Boeddinghous[1] in 1889. They found that the valeroximidolacton of Rischbieth, which is made by treating isonitrosovalerianic acid (made from levulinic acid and hydroxylamine) with concentrated sulphuric acid, to be identical with methyl succinimid, both in melting and boiling points and to give succinic acid and methylamine on treatment with caustic potash.

Methyl Succinimid.



γvaleroximidolacton.



The only conclusions that can be drawn from this remarkable reaction are that either the formula given above for methyl succinimid is wrong or, as is more probable, that the compound must undergo an elaborate molecular rearrangement.

The substitution of a bromine in one of the CH_2 groups of succinimid, was accomplished by Kusserow[2] in 1889. He formed bromsuccinimid $C_2H_3Br(CO)_2NH$ by heating water-free succinimid and bromine dissolved in chloroform in a sealed tube at 120°–130° C. After heating for two or three hours the bromine disappears and the substitution product is seen as a brown oil under the chloroform. $C_2H_4(CO)_2NH + 2Br = C_2H_3Br(CO)_2NH + HBr$.

If water is present and the tube is heated to 160° a mass of white crystals results and scarcely any pressure. The bromsuccinimid is attacked by the hydrobromic acid and water as follows:

$C_2H_3Br(CO)_2NH + 2H_2O + HBr = C_2H_3Br(COOH)_2 + NH_4Br$.

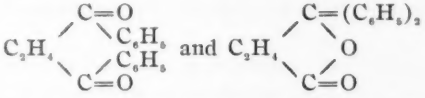
Anilidosuccinimid, $C_2H_3(NH\ C_6H_5)(CO)_2NH$, is formed by warming monobromsuccinimid with an excess of anilin on the

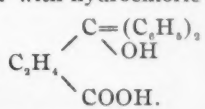
[1] *Ann. Chem.*, (Liebig), **251**, 316, *1889*.
[2] *Ann. Chem.*, (Liebig), **252**, 158, *1889*.

water-bath; from this the following compounds have been made: nitrosoanilidosuccinimid $C_2H_3(N{-}NOC_6H_5)(CO)_2NH$ and acetylanilidosuccinimid $C_2H_3(NC_2H_3OC_6H_5)(CO)_2NH$.

Anilido succinanil $C_2H_3(NHC_6H_5)(CO)_2NC_6H_5$ is formed by warming monobromsuccinic acid with an excess of anilin and recrystallizing the product from alcohol. The corresponding nitroso-compound and the amic acid have also been prepared.

The only investigation pointing towards the existence of an unsymmetrical as well as a symmetrical succinimid is that of Auger.[1] He succeeded in preparing two succinimids by the reaction of ammonia on succinyl chloride in the proportion of eight of the unsymmetrical to one hundred of the symmetrical. He also formed the silver salt corresponding to the silver salt of symmetrical succinimid, but failed to make the unsymmetrical succinimid. Auger's investigation on the imid is very imcomplete so that to draw any inference as to the molecular arrangement of succinimid, we must consider his work on succinyl chloride and phtalimid. Succinyl chloride when acted on by benzene and aluminum chloride in the cold for five hours, gives a mixture of a symmetrical and unsymmetrical compound.

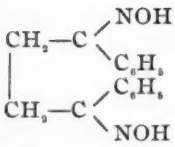


The unsymmetrical compound melts at 90° C., is insoluble in water and cold alkalies, and has a neutral reaction. When treated with potash on the water-bath and then made acid with hydrochloric acid γdiphenyloxbutyric acid separated out, 

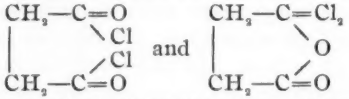
as we would expect from the lactone formula, this body melts at 145° and gives water and the unsymmetrical lactone, M. P. 90° C.

The symmetrical body, separated from the unsymmetrical by fractional distillation, is formed in much smaller quantity. It melts at 134° C. and is unacted on by alkalies. Its symmetrical constitution is shown by the formation of a dioxime.

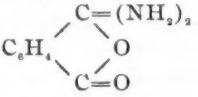
[1] *Ann. chim. phys.*, [6] **22**, 289-368, *1891*.



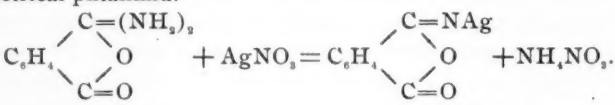
These results show that succinyl chloride is a mixture of the symmetrical and the unsymmetrical.

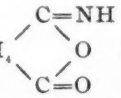


If there are two succinyl chlorides, it would seem that there should be two succinimids and the probability of the existence of the unsymmetrical, at present unknown, is more evident by Auger's research on the amids of phtalic acid.

Unsymmetrical phtalamid  is formed by dropping phtalyl chloride into a large excess of aqueous ammonia, then evaporating, drying, and extracting with ninety-nine per cent. alcohol and recrystallizing. It begins to melt at 90° C. and is soluble in water while the symmetrical phtalamid is not.

The unsymmetrical compound gives a silver salt having the composition $C_6H_4O_2NAg$ which is the silver salt of the unsymmetrical phtalimid.



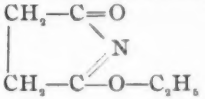
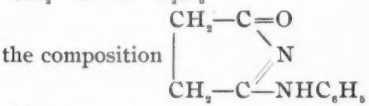
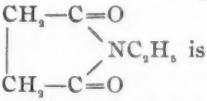
The unsymmetrical phtalimid  is made as follows: To a seven per cent. aqueous solution of the unsymmetrical phtalamid add, in the cold, a quantity of hydrochloric acid calculated to remove one NH_3. A voluminous white precipitate is the immediate result, which, when recrystallized from ninety-five per cent. alcohol, gives a compound which has the same percentage composition as phtalimid, the same appearance,

the same solubility in water, the same acid reaction, and if heated very gently, has the same melting point. But if it is heated rapidly, to about 145° C., it melts, giving a perfectly limpid liquid which in about half a minute, without the disengagement of any gas or vapor, solidifies completely and does not melt till 228° C. is reached, the melting point of the symmetrical phtalimid. It therefore seems that on heating it has undergone a molecular rearrangement and has been converted into the more stable sym-

metrical phtalimid .

The unsymmetrical phtalimid, though similar to the symmetrical in most of its properties, is more easily decomposed by water giving first the amic acid and then the ammonium salt.

The oxygen ethers of succinimid isomeric with the nitrogen ethers previously described, have been prepared recently by Comstock and Wheeler,[1] as follows:

Oxygen ethyl-succinimid. Dry silver succinimid was allowed to stand for several weeks at the ordinary temperature with one molecule of ethyl iodide, diluted with three times its weight of dry chloroform; a dark oily residue was obtained which, when distilled under diminished pressure, gave the ether. It must have the composition  as it gives with anilin a base, having the composition  Some of the nitrogen ether  is formed at the same time, as is proved by allowing the mixture to stand for some time with water, which converts the oxygen ether into succinimid, and then distilling with caustic potash; the distillate showed the presence of primary amine by the isonitril reaction.

[1] *Am. Chem. J.*, 13, 520, *1891*.

The nitrogen ether so obtained agrees in properties with that described by Menshutkin. Oxygen propyl-succinimid was made in the same way, also the isomeric nitrogen ether. The oxygen propyl ether as well as the ethyl ether gives with anilin the base $C_{10}H_{10}N_2O$, melting point 216° C.

Succinimid bromide has been made by Lengfeld and Steiglitz[1] by adding bromine to a solution of succinimid in sodium hydroxide cooled by ice; the yield is ninety to ninety-five per cent. of the theoretical. The melting point is 172.5°; acids instantly liberate bromine and regenerate succinimid; water decomposes it slowly; when pure and dry, it is stable. It is evidently analogous to the succinimid iodide of Bunge, and the succinimid chloride of Bender.

The above compound sometimes called bromyl succinimid was made in the same year by Seliwanow[2] from succinimid and bromyl-acetamide; he gives its melting point as 161°–162° and states that it can also be made from succinimid and hypobromous acid; in the presence of water it acts like hypobromous acid, as does the corresponding chlorine compound. He regards the compound as an amide of hypobromous acid.

It only remains for me to describe here briefly, three new methods by which I have made succinimid.

No. 1. On heating together ethylene cyanide and acetic acid in a sealed tube for eight hours at a temperature of 180°–200° C. the following reaction takes place:

$$C_2H_4(CN)_2 + CH_3COOH = C_2H_4(CO)_2NH + CH_3CN.$$

No. 2. On heating under the same conditions succinic acid and acetonitril, succinimid is formed as follows:

$$C_2H_4(COOH)_2 + CH_3CN = C_2H_4(CO)_2NH + CH_3COOH.$$

No. 3. On heating in the same way equal molecules of succinic acid and ethylene cyanide, two molecules of succinimid are formed, the yield being nearly theoretical.

$$C_2H_4(COOH)_2 + C_2H_4(CN)_2 = 2C_2H_4(CO)_2NH.$$

[1] *Am. Chem. J.*, **15**, 215, *1893*.

[2] *Ber. d. chem. Ges.*, **25**, 3623, *1892*, and *Ber. d. chem. Ges.*, **26**, 423, *1893*.

PART II.

MY EXPERIMENTS ON SUCCINIMID.

First Method. Ethylene Cyanide and Acetic Acid.—Tube No. 1. Three grams of ethylene cyanide (one molecule) were dissolved in 2.25 grams of glacial acetic acid (one molecule) in a small thick glass tube, then a few drops of acetic anhydride were added to render the acid anhydrous; the tube was sealed and heated for two hours at 120°–130° C. and then as no change seemed to have taken place, for six hours at 200° C. On cooling, the tube contained a thick brown liquid.

When this tube was opened several months later, some pressure was observed but no colored flame; the contents were transferred to an evaporating dish and allowed to evaporate slowly. Crystals soon made their appearance, and the entire mass finally turned solid and smelled strongly of acetic acid. To determine a method of purification the solubility of the product was tested as follows:

	Cold.	Hot.
Ether, partially soluble		same
Chloroform, partially soluble		same
Ethyl alcohol, soluble		very soluble
Methyl alcohol, very soluble		very soluble
Benzene, slightly soluble		soluble
Amyl acetate, slightly soluble		same
Carbon disulphide, readily soluble		same
Water, very soluble		same

The mass was dried and extracted with dry ether in a continuous extractor for several hours. On allowing the ether extract to cool, diamond-shaped crystals formed, which were removed and their melting point found to be 123°–124° C. (uncorrected). The ether solution was evaporated to dryness and recrystallized from methyl alcohol, giving white crystals melting at 122.5°–123° C.

These crystals were tested for nitrogen by the prussian-blue reaction, which showed that it was present without doubt. They were also tested with methyl orange in aqueous solution and gave a very light pink, showing that it was neither strongly acid nor alkaline. Comparative tests were made with both cyanacetic acid and succinimid, and the color was found to be almost identical with the latter.

Combustions for carbon, hydrogen and nitrogen were made on some of the best crystals as follows: Nitrogen combustion: weight of substance 0.1211 gram gave 15.15 cc. of nitrogen at a temperature of 23.5°, barometer 769.5 mm.; 14.23 per cent. Carbon and hydrogen determination: weight of substance, 0.1509 gram; weight CO_2, 0.2554; weight H_2O, 0.0760, equivalent to 45.98 per cent. carbon and 5.59 per cent. hydrogen.

As the amount of the recrystallized substance was very small, these combustions could not be checked but some more of the substance had to be prepared as is described later.

Tube No. 2 contained three grams of ethylene cyanide, 4.5 grams of glacial acetic acid and a few drops of acetic anhydride, or one molecule of the cyanide to two of the acid. This tube was treated exactly like No. 1, and the only noticeable difference was that its contents, on evaporation, smelled more strongly of acetic acid, and required longer heating before they solidified, owing to the presence of the greater excess of acetic acid.

The melting point of the crystals from this tube, when purified by crystallization from methyl alcohol, was found to be 123° C. (uncorrected).

A nitrogen determination on crystals from tube No. 2 gave the following figures: Weight substance, 0.2026 gram; volume of nitrogen, 25.5 cc. at 22° C., and 772.5 mm., 14.44 per cent.

The carbon and hydrogen were determined as follows: Weight substance, 0.3303 gram; weight CO_2, 0.5857 gram; weight H_2O, 0.16055 gram, equivalent to carbon 48.36 per cent., and hydrogen 5.39 per cent.

I considered that this substance was identical with that obtained from tube No. 1 and that it was probably succinimid.

The following table shows a comparison of my first results with the calculated percentage of succinimid:

	Tube No. 1.	Tube No. 2.	Succinimid.
C	45.98	48.36	48.48
H	5.59	5.39	5.05
N	14.23	14.44	14.14
M. P.	123°–124° (uncorrected.)	123° (uncorrected.)	124°—125° (according to different authorities.)

As the yield from tube No. 2 was slightly larger than from

tube No. 1, some more of the substance was made for further investigation by using two molecules of acetic acid to one of ethylene cyanide.

Tube No. 3 contained ethylene cyanide, twelve grams, acetic acid, sixteen grams, acetic anhydride, five drops, and was heated for three hours at 170°–180° C. and then for six hours at about 200° C. The appearance of the tube on cooling was the same as Nos. 1 and 2.

Thinking that, if succinimid was produced, acetonitril must also be formed, an endeavor was made to separate by distillation the more volatile contents of the tube before transferring them to an evaporating dish; and by using a paraffin bath, a few cubic centimeters of a liquid which smelled of acetic acid and acetonitril, were obtained.

The contents of tube No. 3, after evaporating, were extracted with dry ether for five hours and yielded twelve grams of good dry crystals (theory, 14.85 grams). A portion of these crystals was purified by crystallization from methyl alcohol and combustions were made on it as follows: Nitrogen determination: Weight substance, 0.1923 gram; volume of nitrogen, 24.6 cc.; temperature, 25° C.; pressure, 771 mm.; 14.34 per cent. nitrogen. Carbon and hydrogen determination: Weight substance, 0.2948 gram; weight CO_2, 0.5264 gram; weight H_2O, 0.1416 gram; 48.69 per cent. carbon; 5.33 per cent. hydrogen.

These figures agree closely with the percentage composition of succinimid, but to confirm them some of the crystals were treated with boiling aqueous caustic potash; ammonia was given off and succinic acid was formed, which was obtained by extracting with ether, and its melting point determined. This agreed with the established melting point of succinic acid. The reactions are as follows:

$$\begin{array}{l} CH_2{-}C{=}O \\ \quad\quad\quad\quad\ \ NH + 2KOH = \\ CH_2{-}C{=}O \end{array} \begin{array}{l} CH_2{-}COOK \\ \quad\quad\quad\quad + NH_3 \\ CH_2{-}COOK \end{array}$$

$$\begin{array}{l} CH_2\,COOK \\ \quad\quad\quad + H_2SO_4 = \\ CH_2\,COOK \end{array} \begin{array}{l} CH_2\,COOH \\ \quad\quad\quad + K_2SO_4. \\ CH_2\,COOH \end{array}$$

Another portion of the pure crystals was tested for reduction

to pyrrol as follows: A small portion of the crystals was ground fine with zinc dust in an agate mortar, and the mixture then transferred to a very small distilling flask and heated over a Bunsen burner; the distillate was but a few drops, but the fumes turned a piece of pine moistened with hydrochloric acid bright red, showing unmistakably the presence of pyrrol.

Reaction is $\begin{matrix} CH_2—C=O \\ | \quad\quad\quad NH \\ CH_2—C=O \end{matrix} + 2H_2 = \begin{matrix} CH=C—H \\ | \quad\quad\quad NH \\ CH=C—H \end{matrix} + 2H_2O.$

Some of the crystals obtained from tubes 1, 2, and 3 are large and diamond-shaped when crystallized from ether and retain this characteristic diamond form even when recrystallized from methyl alcohol.

The lack of agreement in the melting points of succinimid and my crystals is explained by the length of the column of mercury outside the liquid in which the melting point was determined. The correction for this was found to be 1.8°, which would make my results agree with the accepted melting point of succinimid. To make sure that there was no mistake in this determination the melting point of some succinimid, made by the distillation of ammonium succinate, was found by my thermometer under the same conditions as obtained in the previous determination, to be 123° C.

Second Method. Acetonitril and Succinic Acid.—This method was tried to see whether the position of the COOH and CN groups had any effect on the reaction.

Tube No. 4. Succinic acid, 17.7 grams (one molecule), acetonitril, 12.3 grams (two molecules), and acetic anhydride four drops, were heating in a sealed tube for eight hours as described under tube No. 3. On cooling, this tube contained a black liquid but not as thick as the preceding. The contents were evaporated and extracted as before. Crystals were obtained which melted at 123° but were not entirely diamond-shaped. The yield in this case was nine grams but would probably have been larger had the tube been heated longer.

The pure crystals from this tube were treated with hot KOH and gave ammonia and succinic acid which was identified by its

melting point. They also gave pyrrol when distilled with zinc dust as in the previous case. Combustions for carbon, hydrogen and nitrogen were made with the following results:

Carbon and hydrogen: Weight substance, 0.2857 gram; weight CO_2, 0.5080; weight H_2O, 0.1382; equivalent to carbon, 48.49 per cent.; hydrogen, 5.37 per cent. Nitrogen: weight substance, 0.2787 gram; volume of nitrogen, 36.45 cc. at 27° C. and 766 mm.; pressure, equivalent to 14.54 per cent. nitrogen. (This figure is too high as NaOH was used to absorb the CO_2 because the KOH had given out.)

The crystals from this tube are undoubtedly identical with those obtained from Nos. 1, 2, and 3, and are formed according to the following reaction:

$$CH_3CN + (CH_2COOH)_2 = (CH_2)_2(CO)_2NH + CH_3COOH.$$

The second molecule of acetonitril plays no part in the reaction but was used to make the experiment as far as possible the reverse of No. 3.

I had hoped that these experiments might throw some light on the molecular arrangement of succinimid, but think they have not. Though the succinimid produced is undoubtedly identical with that formed by the distillation of ammonium succinate, and is probably symmetrical on account of its reduction to pyrrol, and is formed invariably to whichever radical the cyanogen group is attached, still I think, considering the analogy of phtalimid, that if an unsymmetrical succinimid were produced at first, that under the conditions of heat and pressure it would be converted into the more stable symmetrical compound.

Third Method. Ethylene Cyanide and Succinic Acid.—Tube No. 5 contained ethylene cyanide, eight grams, (one molecule); succinic acid, 11.8 grams, (one molecule); acetic anhydride, two drops. This tube was heated for six hours at a temperature of about 200° C. On opening, considerable pressure was observed and the contents were solid and semi-crystalline. The hard mass was extracted with ether as before; the crystals were partly diamond-shaped and partly rhombic octahedra; some had flat, diamond-shaped bases, and a pyramid on top, showing that the diamond-shaped crystals were but modifications of the rhombic octahedra, the ordinary crystalline form of succinimid.

According to the reaction

$$\begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} + \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} = 2 \begin{array}{l} CH_2C{=}O \\ | \quad \diagdown\!\diagup NH \\ CH_2C{=}O \end{array}$$ the

theoretical yield would be 19.8 grams. 16.2 grams, or 81.8 per cent. of the theoretical were obtained. The residue of carbon weighed 1.7 grams, which would be equivalent to 3.5 grams of succinimid, so that the loss due to manipulation was only 0.1 gram.

Two determinations of the melting point of the succinimid from this tube gave 122° C., or corrected, 123.8° C. The crystals also gave on distillation with zinc dust, pyrrol as before. Prof. Moses, of the School of Mines, very kindly measured the crystals obtained. The results were as follows:

$$a : b : c = 0.8044 : 1 : 1.471.$$

Some allowances must be made on account of the hollow faces of these crystals in comparing these figures with those of Bunge:[1]

$$a : b : c = 0.7888 : 1 : 1.3655.$$

Molecular Weight Determinations.—In order to determine that the molecular weight of succinimid was not a multiple of that ascribed to it (99), it was determined by Raoult's method, using water and glacial acetic acid as solvents. The method pursued was that given in Wiedermann and Ebert's Physikalisches Praktikum, Braunschweig, 1890.

First determination. In this experiment water was used as a solvent; the freezing mixture was snow and hydrochloric acid; the substance used was made by the action of acetonitril on succinic acid (tube No. 4).

The thermometer was set for water by changing the amount of mercury in the column, and then the freezing point of distilled water was determined twice. Both determinations gave 2.40 on the Beckman thermometer. 8.0449 grams of water were used which filled the portion of the tube in the freezing mixture; after the second determination the ice was allowed to melt and 0.1146 grams of the substance introduced through the side tube; when this had dissolved completely, which required an hour and a half, the mixture was again chilled; the mercury went down gradually to 0.8° and then rose rapidly to 2.12° where it remained

[1] *Ann. Chem.*, (Leibig), Suppl., 7, 118, *1870.*

stationary for some time; after making sure that this was the correct reading, the mixture was allowed to melt and a second addition of 0.1153 gram of substance introduced as before. The process was repeated and the freezing point found to be 1.84°; using for water the value 18.5, the calculation is as follows:

$M = \frac{I'}{e}$ or M, the molecular weight, is equal to the constant determined for water by use of known substances divided by e the depression in degrees centigrade produced by one gram of the substance dissolved in 100 grams of water. To obtain e we have the following proportions for the first addition:

$$0.1146 : 8.0449 :: X : 100.$$

X, number of grams per hundred grams of solvent in the solution used, 1.424.

$$1.4245 : 1 :: 0.28 : e \qquad e = 0.1965°$$

Substituting in formula $M = \frac{I'}{e} = \frac{18.5}{0.1965}$ or $M = 94.1$. For the second addition:

$$0.2299 : 8.0449 :: X : 100 \qquad X = 2.8577$$
$$2.8577 : 1 :: 0.56 : e \qquad e = 0.1959° \quad M = 94.4$$

Though the results were sufficiently accurate to show that the formula of succinimid was not a multiple of ninety-nine, further experiments were made to confirm them and to obtain results with some other solvent as a check.

Benzene was tried but though a much smaller amount of substance was used, it was not sufficiently soluble to give any satisfactory results. On chilling the mixture, the succinimid gradually separated out and the thermometer did not go down regularly below the freezing point and then rise to and remain at a definite place, but went down continually by jerks. In determining the freezing point of benzene, snow and a little salt was used and it was found inadvisable to have the freezing mixture more than 10° below the freezing point of the solvent.

Ethylene bromide was next tried but exactly the same difficulty was encountered as with benzene. Water was again used as a solvent and the following figures were obtained with crystals from tube No. 3.

Weight of solvent, 9.6352; freezing point, 4.72°.

First addition: Weight substance, 0.0536; freezing point, 4.626°; e = 0.1689; M = 109.4.

Second addition: Weight substance, 0.0536 + 0.0568 = 0.1104; freezing point, 4.55°; e = 0.1485; M = 124.6.

Third addition: Weight substance, 0.0536 + 0.0568 + 0.0586 = 0.1690; freezing point, 4.395°; e = 0.1853; M = 99.8.

Fourth addition: Weight substance, 0.2224; freezing point, 4.22°; e = 0.2168; M = 85.3

Determinations. Using Acetic Acid.—99.5 per cent. acetic acid was used in this work and the figure 38.6 (taken from Ostwald on Solution, page 229) was employed. A new difficulty was encountered in these determinations, which was that the acetic acid froze at a lower temperature each time; successive determinations gave the following figures: 2.17°, 2.13°, 2.105°, 2.08°. The explanation of this is that the acetic acid is constantly becoming weaker and the greater proportion of water gives a lower freezing point. In making the determination it was therefore necessary to estimate the probable depression due to evaporation and subtract it from that observed.

The determination was made substantially as before except that cold water was used instead of the freezing mixture. As the lowering of the freezing point of the acetic acid seemed to grow slightly less on successive freezings, the probable freezing points for the next three determinations were estimated at 2.055°, 2.035°, and 2.015°, respectively. Weight of acetic acid, 12.1795 grams; weight of substance (succinimid from tube No. 3), 0.0700.

Second determination on first addition: Freezing point 1.81°; e = 0.3893; M = 99.1. Second addition: Weight solvent, 12.1795 grams; weight of substance, 0.0700 + 0.0965 = 0.1665; freezing point, 1.50°; depression, 0.515; e = 0.3840; M = 100.5.

The average of two determinations on substance from tube No. 4 is 94.25, using water as the solvent.

The average of four determinations on substance from tube No. 3 is 104.8 (solvent water).

The average of two determinations on same, using acetic acid as the solvent, is 99.8.

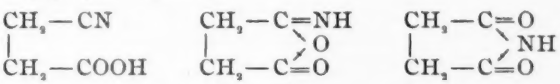
General average, 99.61.

Conclusions.—Succinimid has been made as follows:

1. By the action of ammonia on succinic anhydride. (D'Arcet.)
2. By passing ammonia over melted succinic acid. (Fehling.)
3. By the distillation of ammonium succinate. (Fehling.)
4. By the distillation of acid ammonium succinate. (Fehling.)
5. By the distillation of succinic acid and acetamide. (Menshutkin.)
6. By heating ethylene cyanide and acetic acid in a sealed tube.
7. By heating in the same way acetonitril and succinic acid.
8. By heating, as above, ethylene cyanide and succinic acid.
9. Methyl succinimid has been made by the action of sulphuric acid on isonitrosovalerianic acid.

There seems to be no doubt that the succinimid produced by all these methods is identical. Its molecular weight and percentage composition show that the formula must be $C_4H_5NO_2$.

For its molecular arrangement, we have to choose between the following graphic formulae:



The first is inadmissible as it is shown by Landsberg that the ethyl ether on decomposition gives ethylamine, while the ethyl ether of β cyanpropionic acid would give ethyl alcohol; it also seems to me that β cyanpropionic acid would turn methyl-orange pink as cyanacetic acid does, but as succinimid does not.

Between the last two, the facts that succinimid on reduction with zinc dust gives pyrrol and with alcohol and sodium pyrrolidin and that succinimid is formed invariably to whichever radicle the CN and COOH groups are attached, are the most important evidences in favor of the symmetrical arrangement. We would also expect that the symmetrical would be the more stable compound. This is borne out by the well-known stability of succinimid, which can be distilled without decomposition.

I believe that succinimid is symmetrical as all the facts observed point to that conclusion; but I think it cannot be proved absolutely until its specific refractive power is determined, which will show in connection with the specific refractive powers of the other elements and with that of nitrogen when

joined in different ways, whether, in the case of succinimid, it is attached to one or two carbon atoms.

If β cyanpropionic acid could be isolated, it might on heating be converted into the isomeric unsymmetrical succinimid, and it was with a view to this that the attempts to make this acid, described in part third, were undertaken.

PART III.

ATTEMPTS TO MAKE AND ISOLATE β CYANPROPIONIC ACID BY THE ACTION OF POTASSIUM CYANIDE ON β IODOPROPIONIC ACID.

No. 1. Seventy-five grams of β iodopropionic acid were dissolved in ninety cc. of hot water and neutralized with thirty-four grams of potassium carbonate, then thirty-five grams of finely pulverized potassium cyanide were added and the solution stirred till it dissolved. It was next evaporated and stirred continuously with a thermometer till the temperature reached 132° C. During this time some hydrocyanic acid was given off; the mass was dissolved in a little hot water and neutralized with hydrochloric acid, then evaporated on a water-bath to a syrupy mass and shaken with ether. The ether extract on evaporation yielded nothing.

Before the experiment could be repeated, it was necessary for a new supply of β iodopropionic acid to be made from glyceric acid, and as no phosphorous di-iodide was to be obtained, that had to be prepared also.

After having secured a supply of the iodo acid, the attempts to convert it into the cyan acid were resumed.

No. 2. Fifty grams of β iodopropionic acid were dissolved in a little hot water and 22.8 grams of finely pulverized potassium carbonate added and the carbonic acid boiled out; 21.66 grams of potassium cyanide were dissolved in as little hot water as possible and added to the solution now containing the potassium salt of β iodopropionic acid. The solution was allowed to stand over night and then boiled with a return condenser for five

hours, in an endeavor to ensure the formation of KI and cyanpropionic acid. The liquid was then put in an evaporating dish and neutralized with a calculated quantity of normal sulphuric acid and shaken with ether many times, the ether being recovered and used repeatedly, the residues from which the ether was distilled, were dissolved in water and shaken with lead carbonate separately. This gave an effervescence showing the formation of the lead salt of an acid and also of some lead sulphate. These several mixtures were each filtered and then saturated with hydrogen sulphide to precipitate the lead and set free the cyan acid. The lead sulphide was filtered out and the solution evaporated as far as possible on a water-bath. It was then put in a desiccator under diminished pressure over sulphuric acid and left for twenty-four hours. At the end of that time needle-like crystals appeared; they were left there for several days longer and the crystals were subsequently removed and dried between filter paper.

The crystals were white and small and not over 0.100 gram in weight. This method seemed an improvement over the use of hydrochloric acid but the yield was so extremely small as to be rather discouraging.

No. 3. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate added until the solution was alkaline. It was then warmed on a water-bath till the effervescence ceased when nine grams of freshly pulverized potassium cyanide were added and the mixture heated till it was dissolved. In this way the amount of water present was reduced to a minimum. It was evaporated to a syrup on a water-bath and heated over a flame until the temperature reached 125° C. It was next transferred to a beaker and made acid by the addition of three cc. of concentrated sulphuric acid previously diluted with water. Carbon dioxide was given off as before. It was then shaken with large quantities of ether to extract the free acid and let stand for four weeks before the ether was distilled off. The residue was similar to that obtained by No. 2, but the quantity was very small.

No. 4. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate was added until the

reaction was alkaline, which required 19.75 grams owing to the poor quality of the iodo acid used. 11.4 grams of finely ground potassium cyanide were added and the solution warmed till it dissolved. The solution was at this time straw colored and was heated to boiling and boiled for about a minute, when it became dark reddish brown and smelled of hydrocyanic acid. The heating was stopped here, as the destruction of the compound by overheating was feared.

8.12 cc. of concentrated sulphuric acid diluted with thirty cc. of water were added which gave a lively effervescence of hydrocyanic acid. It was evaporated carefully over a flame and the sticky mass put in a continuous extractor and extracted for several hours. The ether was finally evaporated and the yellowish crystalline residue was dissolved in methyl alcohol which was put aside to crystallize. From this lot were obtained 0.200 gram of good crystals.

No. 5. The same method was tried again but the mass was heated to 135° instead of 125° and the acid was not added until after the evaporation. Twenty-five grams of β iodopropionic acid of good quality were dissolved in twenty-five cc. of hot water and neutralized with 10.15 grams of finely pulverized potassium carbonate; after it was warmed to drive out carbon dioxide, 11.35 grams of ground potassium cyanide were added. The mixture was placed on the water-bath to react for three hours. It was then heated over a flame until the temperature reached 135° after which it was allowed to cool and 4.17 cc. of concentrated sulphuric acid diluted with fifteen cc. of water were added. There was some smell of hydrocyanic acid but not so much as in No. 4. This was next evaporated rapidly over a flame till the mass was only slightly sticky, transferred to an extractor and extracted with ether for four hours. The residue was tested and found to be potassium cyanide and iodide. The ether solution was distilled and the residue recrystallized from methyl alcohol as before. The yield was small as usual.

No. 6. The effect of pressure as well as heat was tried in this and the following experiment:

Two lots of ten grams each of β iodopropionic acid were weighed out and mixed with 3.46 grams of fine potassium car-

bonate. To this, water was added and the whole warmed until it dissolved. Then 3.28 grams of potassium cyanide were dissolved in water and added to each, and the resulting solutions put in tubes. On standing, the solutions became dark colored; they were sealed and heated for three hours at 112° C., then allowed to cool. A black film appeared on the inside of the tubes similar to that deposited on the flask when boiled with a return condenser. They were heated three hours longer at the same temperature and examined; the contents seemed to be turning solid. The tubes were heated again for seven hours and when opened there was no perceptible pressure.

The contents of the two tubes were combined and evaporated on a water-bath to a syrup and enough sulphuric acid added to neutralize all the potassium carbonate. There was no effervescence whatever which was encouraging as it indicated that the potassium cyanide had been converted into iodide. It was replaced on the water-bath to evaporate, and when dry, extracted in a continuous extractor for six hours. The ether was then distilled and the residue of nearly white needle-shaped crystals dissolved in methyl alcohol and set aside to crystallize. After four days the crystals were dried and their melting point was found to be 165°. The yield was 0.658 gram; theory, 5.1.

No. 7. This experiment differs from the preceding in that two molecules of potassium cyanide were used instead of potassium carbonate; one to form the potassium salt of the acid and the other to furnish the CN group.

Two portions of five grams each of β iodopropionic acid were weighed out, and to them were added 3.28 grams of potassium cyanide, dissolved in eight cc. of water. This produced an effervescence of hydrocyanic acid. It was transferred to tubes and allowed to stand for several hours, during which time the solution became dark reddish brown in color. These tubes were heated the same as No. 6 and appeared about the same. They were combined and evaporated as before, and enough of sulphuric acid added to satisfy one-half the potassium cyanide. The contents of the two tubes were extraced with ether as previously described, the crystals looked about the same as those obtained by No. 6 and melted at 162° C. The yield was 0.175 gram; theory, 2.9 grams.

ATTEMPTS TO MAKE β CYANPROPIONIC ACID FROM ETHYL ETHER OF β IODOPROPIONIC ACID.

No. 8. As the ethyl ether of chloracetic acid on treatment with potassium cyanide gives cyanacetic acid, it seemed probable that the ethyl ether of β iodopropionic acid would give β cyanpropionic acid. It was with this hope that the following experiments were undertaken.

The iodo acid had first to be converted into the ether which was done as follows: 200 grams of β iodopropionic acid, 100 grams of ethyl alcohol, and twenty grams of sulphuric acid were mixed in a round-bottomed flask and heated on a water-bath with a return condenser for five and a half hours. The liquid had then separated into two layers. It was transferred to a separator and washed, first with sodium carbonate solution and then with water. The ether, a dark, heavy liquid, was then separated and dried. The yield was 125 grams.

To convert the ether into the cyan acid I used an excess of potassium cyanide over the two molecules required by the reaction.

$$CH_2ICH_2COOC_2H_5 + 2KCN = CH_2CNCH_2COOK + KI + C_2H_5CN.$$

To 145 grams of the ether were added ninety-three grams of potassium cyanide dissolved in 372 grams of water. This mixture was made in a round-bottomed flask in which it was left to stand for twenty hours, the ether forming a separate layer. It was then heated with a return condenser for ten hours; at the end of five hours the layers had mixed and the whole solution was a dark brown in color. On removing from the flask, a dark oil was seen floating on the liquid and to obtain this it was shaken with ether twice, the ether extracts separated, and the ether distilled off; the residue was a brown oil which was tested for nitrogen by the prussian blue reaction but none was found. It, however, gave a decisive test for iodine, and was the unaltered ether of β iodopropionic acid.

The solution from which the unaltered ether had been removed was made almost neutral with sulphuric acid and evaporated on a water-bath to dryness. It was then made acid with dilute (normal) sulphuric acid and shaken twice with liberal quantities of ether. The residue, a brown liquid, was made strongly acid

with sulphuric acid and shaken with ether three times. The residue from this treatment was evaporated to dryness on a water-bath and extracted with ether three times more.

The three different ether solutions, supposed to contain the cyan acid, were distilled separately and the residues kept to convert into the lead salt of cyanpropionic acid as a means of purifying the product. To do this they were shaken with lead carbonate in excess and then the lead sulphate and carbonate filtered out. The formation of the lead salt gave a lively effervescence with the first two lots but failed to give any with the third, so I considered that none of the cyan acid was removed by the last extractions.

The filtrates described above were saturated separately with hydrogen sulphide, which gave a copious precipitate of lead sulphide. The solutions were filtered and the filtrates combined and evaporated on a water-bath to dryness. It was then found that the lead had not been entirely removed, so the mass was redissolved in hot water, and hydrogen sulphide passed in again. It was filtered and washed as before and evaporated on a water-bath. On cooling, the substance turned solid.

The solubility of this substance is as follows:

	Cold.	Warm.
Ether	insoluble	almost insoluble
Ethyl alcohol	slowly soluble	soluble
Chloroform	insoluble	insoluble
Carbon disulphide	insoluble	insoluble
Methyl alcohol	insoluble	soluble
Acetone	insoluble	insoluble
Benzene	insoluble	insoluble

Some of this product was recrystallized from both ethyl and methyl alcohol and the melting points determined. The results were as follows:

Ethyl alcohol	110°–111°
Methyl alcohol	109°–110°
Crude	154°

A small sample was recrystallized from methyl alcohol several times and its melting point determined. It began to melt at 117° but part remained solid until 144° was reached, when all melted, indicating in spite of repeated recrystallizations that the sample was a mixture.

No. 9. This method is a slight modification of the preceding. Ninety grams of potassium cyanide were dissolved in 300 cc. of water and added to 142 grams of the ethyl ether of β iodopropionic acid in a round-bottomed flask as before. This was heated on a water-bath with a return condenser for twelve hours to try to ensure the entire conversion of the ether; it was then shaken with ether in a separator to recover the unaltered ether, and in spite of the increased time during which the mixture was heated thirty-five grams of the ether were obtained.

The under layer from the separator was neutralized with sulphuric acid and evaporated on a water-bath to a syrup. It was made acid with dilute sulphuric acid (one to one) and shaken with ether in a separator three times, using liberal amounts of ether each time.

(The object of first neutralizing and afterwards making acid was to avoid as far as possible, heating with acid which might form succinic acid.) The ether solutions were of a dark reddish color, much darker than those obtained in No. 8. The ether was distilled off, the residue diluted with water, shaken with lead carbonate, filtered, washed, the filtrate saturated with hydrogen sulphide as before, the lead sulphide filtered out and the solution evaporated on the water-bath.

The residue from the ether extraction was evaporated on a water-bath until on cooling it turned solid, and was then transferred to a separator and made much more strongly acid with dilute sulphuric acid, and was well mixed and shaken three times with ether. The ether solution was treated as before, and after removing the lead, was added to the first portion and evaporated to dryness with it. The solid mass was then crystallized twice from methyl alcohol.

To the residue from the second ether extraction in the separator, water was added and the solution filtered, the residue was rejected, and to the filtrate, litharge and lead carbonate added until all the acid present which was mostly sulphuric was neutralized. It was next filtered and hydrogen sulphide passed in. A precipitate of a dark red brown color was obtained instead of the black lead sulphide. This precipitate was filtered out and was found to contain lead and sulphur, was soluble in hot

dilute nitric acid and in concentrated hydrochloric acid, but insoluble in dilute sulphuric. This red precipitate sometimes forms at other times when the solution supposed to contain the lead salt of β cyanpropionic acid is saturated with hydrogen sulphide, but it was always either subsequently decomposed or obscured by the quantities of black sulphide which formed later.

This compound is apparently similar to the lead chlorosulphide described by Fresenius (page 173 Qual. Anal.), but in which some organic acid replaces the hydrochloric acid.

The filtrate from this precipitate was evaporated to dryness on the water-bath and extracted with ether four times. The ether was distilled off and the resulting crystals recrystallized from methyl alcohol.

Total yield, 2.6 grams, having a melting point of 124° C.

INVESTIGATION OF CRYSTALS MADE BY THE PRECEDING METHODS.

Combustions were made on the crystals obtained by methods 8 and 9. The amount of moisture was also determined by drying so as to calculate the percentage to the dry if possible. The results were as follows:

No. 8 gave—

Carbon	38.95 per cent.
Hydrogen	6.39 " "
Nitrogen	11.62 " "
Loss on drying for five hours at from 90° to 107°	12.31 " "
Nitrogen, on dried sample	8.07 " "

These results calculated to the dry measure gave—

Carbon	44.42 per cent.
Hydrogen	5.72 " "
Nitrogen	13.25 " "

These combustions were made very carefully and I believe them to be correct. The figures agree quite closely with the percentage composition of $C_8H_{12}N_2O_6$, which is

Carbon	44.44 per cent.
Hydrogen	5.55 " "
Nitrogen	12.97 " "

This might be formed by two molecules of β cyanpropionic acid taking up one molecule of water and combining, $2C_4H_5NO_2 +$

$H_2O = C_8H_{12}N_2O_5$, or it may be written $C_4H_5NO_2 + \frac{1}{2}H_2O$. The melting point of crystals from No. 8, on which these combustions were made, was 110° C.

No. 9 gave—

Carbon	37.15	per cent.
"	37.27	" "
Nitrogen	6.34	" "
"	6.19	" "
Hydrogen	5.77	" "
"	5.79	" "

Loss on drying to constant weight for eighteen hours at 100°–110°, 13.22 per cent.

These determinations of the carbon, hydrogen, and nitrogen, calculated to the dry gave—

Carbon	42.88	per cent.
Hydrogen	4.96	" "
Nitrogen	7.22	" "

A nitrogen combustion was made on the crystals from Nos. 6 and 7, which gave further evidence of the loss of nitrogen by heating as the crystals obtained by these methods contained but 3.02 per cent. nitrogen.

The crystals from methods 8 and 9 were dissolved in water and tested with methyl orange to see whether they would give an acid reaction, but they did not. They only gave the color of a neutral solution. Succinimid (M. P. 124) was tried which gave the same color. Cyanacetic acid was also tried but this gave a bright pink. From this it was evident that the crystals could not be β cyanpropionic acid or they would turn the indicator like cyan acid.

The mother liquor from method No. 5, in which the crystals were slowly forming, was tested in the same way and it gave a decided pink color. To make sure this was not due to any mineral acid, I tested for sulphuric acid with barium nitrate but found none. (Sulphuric was the only acid used in the method.)

I now believe that β cyanpropionic acid is a liquid and is formed in many of the preceding methods, but that it decomposes very readily by heat or pressure, forming various complicated organic compounds, which are the crystals obtained. Another reason for my thinking so is that methods 6 and 7 which

are heated in sealed tubes, on evaporating gave crystals direct, while in the methods which were not heated so much a syrupy liquid was left, which only deposited crystals after standing in some cases for weeks over sulphuric acid, showing the complete decomposition of the acid in the first case and but the partial in the second as it was there the acid reaction was obtained. The irregularity of the combustion is explained by the fact that the samples must have been in most cases, mixtures. The only combustions which agree very well are those made on the same day on a sample of No. 9 which had been recrystallized four times.

The diminished percentage of nitrogen in the methods where longer or higher heat was used, and also where the sample was afterwards dried, seems to be invariable and points to a decomposition in which nitrogen is lost.

The nearest approach to β cyanpropionic acid so far produced is its ethyl ether which has been made by L. Henry,[1] as follows:

Heat $CH_2ICH_2COOC_2H_5$ with potassium cyanide dissolved in alcohol in slight excess on a water-bath with a return condenser. The reaction takes place easily and potassium iodide is deposited abundantly; at the end the liquid turns brown. Drive out as much of the alcohol as possible by distilling on the water-bath and extract the cyan ether with ordinary ether. The distillation of the ether solution gives the pure cyanpropionic ether. The yield is almost theoretical.

The cyanpropionic ether is a colorless liquid, without odor, insoluble in and more dense than water, and boils at 228°. Caustic potash in aqueous alcohol transforms it easily into normal potassium succinate. With aqueous ammonia it gives cyanpropionic amide $CN(CH_2)_2CONH_2$.

The preceding facts were not known to me at the time I made my experiments on iodopropionic ethyl ether or I should have tried alcoholic cyanide, and so by the elimination of water, would have probably succeeded in obtaining the ethyl ether and amide of β cyanpropionic acid, if not the acid.

My experiments show that the β iodopropionic ethyl ether does not act with potassium cyanide like the ethyl ether of chloracetic, as by treating the latter with potassium cyanide as

[1] L. Henry, *Bull d. l'acad. royal de Belgique*, [3] **18**, 168, *1889*.

described under the first method in which the ether was used, I obtained a good yield of cyanacetic acid without difficulty.

The reactions between nitriles and both fatty and aromatic acids will be more fully developed in this laboratory.

ORGANIC LABORATORY, SCHOOL OF MINES,
COLUMBIA COLLEGE, MARCH, 1894.

THE DETERMINATION OF PHOSPHORIC ACID.

BY S. W JOHNSON.
Received April 25, 1894.

THE papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilizers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared and it was evident that further study was needful before the citrate method could be fully trusted for fertilizer work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage,

bone char, phosphatic guano, and phosphate rock, we found that but three citrate determinations differed from those by molybdate, by more than 0.3 per cent., and but four others by more than 0.2 per cent. The greatest discrepancy between the two methods was 0.41 per cent., while the average difference was 0.09 per cent. In thirty cases the citrate method averaged 0.117 per cent. more, in thirty-three cases 0.079 per cent. less, than the molybdate method. These percentages were reckoned on 0.4 gram of substance containing from 0.5 to 31.5 per cent. of P_2O_5. The determinations were not made with unusual care, but were turned off rapidly as a part of the routine work of the station.

The citrate method was found to give unsatisfactory results where iron and alumina were present in considerable quantity, as in case of "Grand Cayman's Rock," "Thomas Gilchrist Slag," and "Keystone Phosphate." A series of trials under varied conditions was made in 1889 with the hope to ascertain the cause of the discrepancies but without success.

Some analyses of the ignited precipitate obtained by the citrate method may be quoted here:

COMPOSITION OF IGNITED "CITRATE PRECIPITATES."

	Bone.	Super-phos-phate.	Grand Cayman's phos-phate.	South Carolina rock.	Bolivian guano.	Dis-solved bone black.
Carbon	0.41	0.19	0.44	0.15	0.48	0.27
Silica	....	0.12	0.40	0.10	0.24	0.19
Calcium oxide	2.59	2.13	2.05	3.21	3.95	2.05
Magnesium pyrophosphate	95.49	96.07	95.66	95.77	94.98	97.83
Ferric and aluminum phosphate	....	....	0.71	0.35	....	0.31
Loss	1.51	1.49	0.74	0.42	0.35	....
	100.00	100.00	100.00	100.00	100.00	100.65

The loss probably consisted in part, of magnesia and in part also of pyrophosphoric acid. It is seen that the ignited precipitates contained from two to four per cent. of lime, that iron and alumina entered into the precipitate in small quantity when these elements were abundant in the original substance, and that where there was little or no loss, the recovered phosphoric acid amounted to from 95 to 97.8 per cent. of the precipitate.

In case of Grand Cayman's phosphate rock, duplicate determinations differed as much as 0.3 per cent., and the variations of duplicates of Thomas Slag and Keystone phosphate were even greater. It was also found that by changing the proportions of the reagents and by using on the one hand moderate and on the other vigorous and prolonged agitation, the quantity of phosphoric acid, reckoned from the ignited precipitate, fluctuated, in case of Thomas slag and Keystone phosphate, $2\frac{1}{2}$ and $3\frac{1}{2}$ per cent., respectively, although by using large quantities of magnesia mixture and of strong ammonia, accordant and high results were realized.

Thus far we employed the modified rapid molybdate method, precipitating from hot solutions and digesting for one hour at 65° C. Finally in 1890 we found that under this procedure, the molybdate method, though satisfactory in absence of ferric, aluminum, and manganese salts, is, in their presence, little better than the citrate method. In case of Keystone phosphate three determinations by Osborne, using the U. S. "official" method gave figures ranging from 45.25 to 46.68 per cent.!

It was therefore necessary to return to the original Sonnenschein method and make the precipitations at 40° to 50° C., during six hours. Six determinations thus carried out by Osborne, gave results from 44.67 to 44.86, the average being 44.82 per cent.

Comparative duplicate trials on a carefully made up solution of known composition with $P_2O_5 = 18.93$ per cent.[1] (from crystallized sodium phosphate) $Fe_2O_3 = 20$ per cent., $Al_2O_3 = 4.72$ per cent., and $MnO = 5.09$ per cent. (from sulphates), yielded Osborne, by the original Sonnenschein method, 18.92 and 18.94 per cent., and by the "official" method 19.26 and 19.26 per cent.!

We proved that with relative excess of nitric acid or relative deficiency of molybdic acid, a portion of phosphoric acid may easily fail to be thrown down. We also found that when precipitation is made hot and digestion is conducted at 65° C., ferric iron, and aluminum, if present, are to some extent included in the yellow precipitate and when this is dissolved in the subsequent treatment with ammonia, they pass into the alkaline

[1] Determined in the usual manner as magnesium pyrophosphate.

solution and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50°, or as high as 65° C. in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.

DOUBLE BROMIDES OF PALLADIUM.

By Edgar F. Smith and Daniel L. Wallace.

Received May 5, 1894.

BONSDORFF (*Poggendorff's Annalen der Physik*, [1], N. F., **19,** 347) was one of the first chemists to attempt the preparation of double halides of palladium with other metals. Beyond mere mention of the fact that he obtained palladium bromide by the action of a mixture of nitric and hydrobromic acids upon the metal, that the resulting compound apparently combined "mit den Bromiden elektro-positiver Metalle," and that he made double salts of it with the chlorides of potassium, barium, manganese, and zinc, we have not discovered any additional literature relating to the above subject. It does not appear that Bonsdorff analyzed any of the double halides obtained by him.

Desirous of finding a salt or salts of palladium suitable for, but as yet not used in atomic mass determinations of palladium, we took occasion to prepare several double bromides of that metal, hoping to find among them one or more which might be available for the purpose.

Very pure metallic palladium was dissolved in nitro-hydrobromic acid. The residue was moistened with hydrobromic acid and repeatedly evaporated to dryness upon a water-bath. The palladium bromide, reddish-brown in color, was only soluble in water containing hydrobromic acid. Weighed quantities of this

dry bromide, with equivalent amounts of the metallic bromides, were dissolved in water containing hydrobromic acid. Upon evaporation, crystalline residues were obtained. These were always dissolved in water and again allowed to separate.

POTASSIUM PALLADIUM BROMIDE.

K_2PdBr_4.

This salt separated from its aqueous solution in shining reddish-brown needles. It is anhydrous. It is very stable and suffers no change on exposure to the air. In analyzing it we determined the palladium by the method suggested by Frenkel, *Ztschr. anorg. Chem.*, **1**, 229. By following this recommendation the bromine can be precipitated by silver nitrate without contamination with palladium.

Analysis.—0.4930 gram dried material gave 0.1045 gram metallic palladium, equal to 21.19 per cent. Pd, and 0.7428 gram silver bromide, equal to 63.79 per cent. Br, while the theoretical requirements of K_2PdBr_4 are 21.12 per cent. Pd and 63.50 per cent. Br. A second portion of substance, weighing 0.2613 gram, was gently heated in a current of hydrogen and, after cooling, the residue was extracted with hot water. Upon evaporating this aqueous solution to dryness, 0.1251 gram of potassium bromide was obtained. This is equal in percentage to 15.58 per cent., while the theoretical potassium bromide in this double salt is 15.45 per cent.

Hoping that by adding bromine to the aqueous solution of the above salt, and digesting the same with this reagent, at a temperature not exceeding 70°, we might possibly get a salt of the formula K_2PdBr_6, we carried out several such experiments. The result was not what was anticipated; the product being really a salt of the simpler type, K_2PdBr_4, with two molecules of water of crystallization, $K_2PdBr_4 + 2H_2O$. It separated in long, dark-brown and shining needles, which on exposure rapidly lose their luster, become dull, and acquire a reddish-brown color. Owing to the rapid loss of water by the crystals, the analytical results do not approach the theoretical requirements as closely as might be expected.

Analysis.—0.3235 gram substance gave 0.0660 gram, or 20.37 per cent. of metallic palladium; 0.4565 gram of silver bromide,

equal to 60.00 per cent. of bromine and 0.0201 gram of water, equivalent to 6.21 per cent. The formula $K_2PdBr_4 + 2H_2O$ requires 19.71 per cent. Pd, 59.2 per cent. Br, and 6.65 per cent. H_2O.

AMMONIUM PALLADIUM BROMIDE.

$(NH_4)_2PdBr_4$

This salt crystallizes in beautiful and quite large olive-brown colored forms which apparently possess an orthorhombic habitus. They are anhydrous and are perfectly stable in ordinary air. They possess about the same solubility as the corresponding potassium salt.

Analysis.—0.2528 gram dry material gave 0.0585 gram metallic palladium, equal to 23.14 per cent., and 0.4090 gram silver bromide, equivalent to 68.82 per cent. of bromine, while the theoretical percentages are Pd = 22.91, and Br = 69.17.

As this salt and the corresponding potassium salt are anhydrous and can be obtained pure without great difficulty, it is our intention to use them in a redetermination of the atomic mass of palladium.

SODIUM PALLADIUM BROMIDE.

We experienced much trouble in getting this salt, and it was only after the solution, containing equivalent amounts of sodium and palladium bromides, was allowed to remain in a vacuum desiccator over concentrated sulphuric acid for some time that it separated out in large deep red colored plates which proved to be very deliquescent. It was therefore necessary to conduct the analysis with imperfectly dried material. Through an accident we are not able to give a result upon the bromine content, and are limited to a presentation of the palladium and water percentages. These are, 19.68 per cent. Pd, and 14.67 per cent. H_2O. A salt of the composition $Na_2PdBr_4 + 4\frac{1}{2}H_2O$ would require 19.25 per cent. Pd, and 14.63 per cent. H_2O.

This salt is very deliquescent and even to a much greater degree than the corresponding double chloride of sodium and palladium.

STRONTIUM PALLADIUM BROMIDE.

The solution of this salt also stood for many days before crystals made their appearance. It consists of short, black prisms, which are stable on exposure to the air.

Analysis.—0.2256 gram air-dried substance gave 0.0366 gram Pd, or 16.22 per cent.; 0.2643 gram silver bromide, or 49.82 per cent. Br, and 0.0679 gram strontium sulphate, equal to 14.09 per cent. strontium.

A second analysis gave 0.0518 gram Pd, or 16.79 per cent.; 0.3595 gram silver bromide, or 49.57 per cent. Br; 0.0861 gram strontium sulphate, equal to 13.29 per cent. Sr, and 0.0544 gram water, corresponding to 17.63 per cent.

A salt of the composition $SrBr_2.PdBr_2 + 6H_2O$ would require

17.11 per cent. Pd
13.99 " " Sr
51.47 " " Br
17.37 " " H_2O

Our deficiency in bromine, we believe, is due to a slight loss of that constituent occurring during the drying process.

MANGANESE PALLADIUM BROMIDE.

This salt is very soluble in water. Like the two preceding salts it only separated from its aqueous solution after long standing. Its crystalline form is apparently like that of the ammonium salt. The crystals are dull-black in color.

Analysis.—0.1829 gram air-dried substance was carefully heated to constant weight in an air-bath. The loss, representing water, equaled 20.39 per cent. The anhydrous residue was then exposed at a moderate temperature to the action of hydrogen gas. On cooling, the mass was extracted with dilute hydrochloric acid. The spongy palladium weighed 0.0331 gram, equal to 18.09 per cent. Pd. The filtrate from the palladium gave 9.29 per cent. of manganese.

These results indicate a salt with the formula $MnPdBr_4 + 7H_2O$, which would require

17.52 per cent. Pd
9.05 " " Mn
20.73 " " H_2O

An effort was made to prepare the double halides of zinc and of cadmium with palladium, but the products crystallized so poorly that the analysis of the same was abandoned.

UNIVERSITY OF PENNSYLVANIA,
April 25, 1894.

AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

By F. P. Venable.

Received April 16, 1894.

A ZIRCONIUM chloride of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a compound.

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetrachloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey[1] has recorded that even with great care to avoid the presence of moisture he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The necessity for the presence of these in the materials used or in the resulting compounds is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with, have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid

[1] *Chem. News.*, 60, 17.

by heating the salt to 60° C. but was not able to obtain a definite compound. Two analyses gave

ZrO_2	0.332	0.485
AgCl	0.661	1.096

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by hydrochloric acid being $2ZrOCl_2.13H_2O$.

Endemann has described basic or oxychlorides $Zr_3O_4Cl_4$, ZrOClOH, and $Zr_8O_8Cl_7(OH)_9$; Troost and Hautefeuille have described others, $Zr_2O_3Cl_2$ and Zr_2OCl_6. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander[1] made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily soluble in water. They were washed with alcohol and for analyses I and II were pressed between filter paper; III and IV were dried over sulphuric acid. The results were as follows:

	I.	II.	III.	IV.
Zr	27.56	25.69	30.11	31.78
Cl	21.58	21.58	23.06	23.80
Loss (H_2O)	50.86	52.78	46.83	44.12

or calculated on a dry basis:

Zr	56.08	54.41	56.63	57.18
Cl	43.02	45.59	43.37	42.82

Again preparations were made as before. I was dried between filter paper, II over sulphuric acid, III was pressed between filter paper and then dried over sulphuric acid, IV was dried a long time over sulphuric acid. The analyses gave the following:

	I.	II.	III.	IV.
Zr	28.52	34.91	37.78	35.69
Cl	21.93	26.09	25.87	21.74
Loss	49.55	39.10	36.35	42.57

or calculated on a dry basis:

Zr	56.93	57.23	59.34	62.14
Cl	43.07	42.77	40.66	37.86

Lastly he allowed a solution of the chloride to evaporate over

[1] Bidrag till kännedomen om Zirkonjord. Inaug. Diss. Lund, *1864*.

sulphuric acid washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

Zr	27.94	28.74
Cl	27.32	26.67
Loss	44.74	42.62

or calculated on a dry basis:

Found		Theory.	
Zr	50.56	50.04	Zr 38.50
Cl	49.44	49.96	Cl_4 61.50

The above results show that his preparations were indefinite oxychlorides or mixtures in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

(1) By washing with a mixture of one part alcohol and ten parts of ether.

(2) By gently heating the salt.

(3) By exposing the finely divided salt at ordinary temperatures in a vacuous desiccator over potash until no hydrochloric acid appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method (2) a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the relation of ZrO_2 to AgCl.

	ZrO_2 :	AgCl
Berzelius determination	1 :	1.991
" "	1 :	2.260
Bailey's method 1	1 :	2.206
" " "	1 :	2.179
" " "	1 :	2.226
" " "	1 :	2.260
" " 2	1 :	2.264
" " " without washing	1 :	2.245
" " "	1 :	2.309
" " "	1 :	2.285
$ZrOCl_2$	1 :	2.350

These preparations are evidently mixtures also.

Hermann[1] states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid and leaving a basic chloride or oxychloride, $ZrCl_4.ZrO_2.18H_2O$ or $ZrOCl_2.9H_2O$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals when heated become white and turbid and are converted into the anhydrous dioxychloride, $ZrCl_4.2ZrO_2$.

The conditions here are inexact and though Hermann may have obtained these compounds he would doubtless find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linnemann[2] maintains that crystallization from hydrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving fifty per cent. of its weight on ignition and therefore very nearly pure $ZrCl_4$ which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken, some along the lines attempted by others, and others by methods not tried before. In all the purified chloride obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, **5**, 551.

In the first experiment this chloride was washed once with water and then put in a desiccator and dried over calcium chloride (porous desiccated). It remained in the desiccator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded on analysis 48.84 per cent. ZrO_2.

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful

[1] Watts' Dict., 5, 1080.
[2] *Chem. News.*, 52, 224.

ignition left a residue of ZrO_2 equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 42.28 per cent., and Cl 24.35 per cent. Although the results in this and the experiment immediately preceding correspond fairly well, they are unsatisfactory as they point either to a mixture of chlorides or an oxychloride of very complicated formula and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent. of ZrO_2. This corresponds very nearly to the formula $ZrCl_4$, and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110° C., and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough, fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100° C. A

more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on various preparations and I regard the facts stated above as showing conclusively that a neutral zirconium chloride can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2:

52.70 52.78 52.63

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, **5**, 551.)

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this separation as thorough as possible by heating, then to change the chloride into oxide by ignition and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporating, as recommended on a water-bath, and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot-water funnel the dissolved chloride can be filtered away from

this insoluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is $ZrOCl_2$ and with it was found, as an impurity, whatever silica the separation by heating failed to remove.

Lastly, my assistant, Mr. Baskerville, has shown that much time and hydrochloric acid will be saved if, in the solutions containing much iron, the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

UNIVERSITY OF NORTH CAROLINA,
April 12, 1894.

SEPARATION OF ZIRCONIUM BY MEANS OF SULPHUROUS ACID.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

WHILE testing the accuracy of the various methods recommended for the estimation of zirconium I was led, because of the analogy of the elements, to try a method commonly used with titanium; *viz.*, prolonged boiling of a potassium bisulphate fusion in dilute solution with sulphurous acid in excess. On application of this method, however, on a solution of zirconium sulphate (prepared by dissolving the hydroxide in sulphuric acid), I failed even after boiling four hours with an excess of sulphur dioxide to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide and then boiled with an excess of sulphur dioxide, after being greatly diluted, a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through all filter papers at my command. Therefore this method could not be used.

But an addition of sulphurous acid to a solution of zirconium chloride, even in a cold acid solution, a dense white precipitate was immediately noted. On boiling with an excess of sulphurous

acid in a neutralized solution, *i. e.*, the hydrochloric acid solution neutralized by ammonium hydroxide until the slight precipitate formed was no longer dissolved on boiling, and this precipitate then taken up with two or three drops of dilute hydrochloric acid, the zirconium was completely precipitated.

The accuracy of the method is seen in the following results:

	Found.	Used.
ZrO_2	0.1074	0.1077
"	0.1078	0.1077
"	0.1043	0.1038
"	0.1070	0.1077
"	0.1047	0.1050

The precipitation took place immediately on addition of sulphurous acid, and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only, and a sulphate would have to be first changed into chloride by precipitation with ammonium hydroxide and re-solution in hydrochloric acid. The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided and it is best to use a fresh solution of sulphurous acid or the sulphur dioxide gas direct.

This method affords an excellent means of separating zirconium from iron. Several experiments were carried out upon solutions containing known amounts of the chlorides of these two metals. The zirconia was precipitated by sulphurous acid, boiled five minutes, and washed four or five times with hot water. The iron was titrated in the filtrate.

The experiments resulted as follows:

	Found.	Used.
ZrO_2	0.1074	0.1070
Fe	0.0825	0.0823
ZrO_2	0.1078	0.1070
Fe	0.0820	0.0823
ZrO_2	0.1043	0.1043
Fe	0.0439	0.0423

This method served for the separation of zirconium and aluminum as well, as may be seen by the following results:

	Found.	Used.
ZrO_2	0.1042	0.1043
Al_2O_3	0.0608	0.0610
ZrO_2	0.1070	0.1070
Al_2O_3	0.0316	0.0305

UNIVERSITY OF NORTH CAROLINA.

ON THE ANALYTICAL PROPERTIES OF IRON PHOSPHIDE AND PHOSPHATE.

By L. M. Dennis and B. S. Cushman.

Received May 17, 1894.

IN the year 1886, Cheever, in an article in the *Transactions of the American Institute of Mining Engineers*, **15,** 448, sought to explain the variation in effect of a definite amount of phosphorus upon the properties of iron and steel by assuming that the phosphorus exists in the metal in two conditions; *viz.*, as phosphide, which is harmful, and as phosphate, which is harmless, or comparatively so. To demonstrate this he used the following method:

"A weighed sample of iron is treated in the cold with a solution of the double chloride of copper and ammonium until the iron is all dissolved, then filtered without washing. The residue of copper, carbon, phosphorus, etc., is next digested at 50° C. for two hours with 100 cc. of a saturated solution of ammonium oxalate, then filtered and washed; the filtrate contains the phosphate of iron; the residue the phosphide."

Later, in the same article, he shortens the method as follows:

"The copper, carbon, phosphorus, etc., residue is shaken in a flask for five minutes with seventy-five cc. of a cold, one per cent. solution of hydrochloric acid (two cc. strong hydrochloric acid to 100 cc. water—free from chlorine), then filtered and washed with water, the filtrate made strongly acid with nitric acid and evaporated nearly to dryness, and the phosphorus precipitated by molybdate solution."

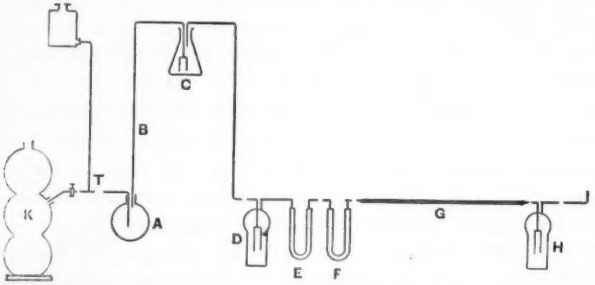
In a second paper in the same Journal, **16,** 269, Cheever gives results obtained by another method, he here volatilizing the iron as chloride by chlorine, "and analyzing the residue for phosphorus, which, if present, must be in the form of phosphoric acid; for the iron phosphide would be volatilized."

At that time doubt was cast upon the accuracy of Cheever's work because of the uncertainty as to the behavior of phosphide of iron towards the different reagents which he employed. In the hope of removing some of that uncertainty the authors entered upon the experimental work detailed below.

Preliminary work upon the phosphides of iron carried out by Mr. Russell Elliott in this laboratory in 1891-2, seemed to show that the different phosphides, of which, according to Freese,[1] there are three, Fe_3P_4, FeP, and Fe_2P, behave quite similarly towards various solvents. For this reason, and also because of the length of time required for the preparation of a pure sample, we prepared and examined only one of the phosphides, selecting that which is formed by treating anhydrous ferrous chloride with phosphine at a red heat.

Ferrous Chloride.—The purest piano wire obtainable was placed in a combustion tube, which was connected on one side with an apparatus furnishing dry hydrochloric acid gas, and on the other side with a Schiff nitrometer[2] filled with strong potassium hydroxide solution. When the air in the tube had been completely displaced by the hydrochloric acid gas, as was shown by the complete absorption of the gas by the caustic potash solution, the combustion tube was heated to redness. The ferrous chloride produced was partly in the form of glistening light-yellow plates, and partly a yellowish amorphous powder. Careful tests showed that it was completely free from ferric chloride.

Phosphine.—The phosphine was generated by the action of a solution of potassium hydroxide upon phosphorus. The form of apparatus finally adopted has given such satisfactory results that a brief description of it may not be out of place. It consists of:



1. The 500 cc. distilling flask A in which the phosphine is generated.

[1] *Pogg. Ann.*, **132**, 225.
[2] *Ztschr. anal. Chem.*, **7**, 430.

2. The upright tube B which serves as a condenser, and which is widened after entering the cooling flask C to prevent its becoming clogged by the condensation of the phosphorus.

3. The cooling flask C which is surrounded with ice-water.

4. The wash-bottle D.

5. The two ⋃ tubes, E and F, filled with calcium chloride for drying the gas.

6. The combustion tube G.

7. The wash-bottle H which prevents the air from diffusing back into the combustion tube.

8. A Kipp apparatus, K, for generating hydrogen.

9. The ⊥ tube T, through which water could be driven into A from the reservoir above in order to stop the generation of the phosphine by diluting the caustic potash solution.

The most uniform evolution of phosphine was obtained by using a 1 : 1 solution of potassium hydroxide, a stronger solution causing a more rapid generation of the gas than was desirable. Although the phosphine resulting from the use of this moderately concentrated caustic potash was not as pure as that obtained with a very concentrated solution,[1] yet the phosphide obtained was probably not influenced to any great extent by the small amounts of hydrogen given off early in the phosphine evolution. The hydrogen would reduce some of the ferrous chloride to metallic iron, but if we accept the statement of Freese,[2] the product is the same whether phosphine acts upon anhydrous ferrous chloride or upon metallic iron. To avoid, however, the production of any unnecessarily large amount of hydrogen the contents of the generating flask was at no time heated to boiling, this precaution serving to lessen the amount of hydrogen arising from the secondary reaction between the potassium hydroxide and potassium hypophosphite:

$$KH_2PO_2 + 2KOH = K_3PO_4 + 2H_2.$$

It was thought that the hydrogen thus set free might reduce the phosphide after the latter had formed, but later experiments with the pure phosphide showed that it was not reduced when highly heated in a current of hydrogen. The solution of potassium hydroxide should be cooled before being poured upon the

[1] A. W. Hofmann, *Ber. d. Chem. Ges.*, 1871, 200.

[2] *Pogg. Ann.*, **132**, 225.

phosphorus in the flask, in order to avoid the immediate generation of any phosphine, as that would cause an explosion upon coming in contact with the air in the flask. As soon as all connections had been made, hydrogen from the Kipp generator was run through the apparatus until all air had been expelled. The sand-bath under the generating flask was then gently heated until the phosphine began to come off somewhat rapidly. The hydrogen was then shut off and the flame removed, the latter being replaced only when the solution of the gas had nearly ceased. This procedure greatly lengthened the duration of the current of phosphine.

When nearly all of the hydrogen had been driven from the apparatus the phosphine burst into flame at the end of the outlet tube. The combustion tube was then heated. As soon as the hydrochloric acid gas, formed by the action of the phosphine upon the ferrous chlorine, began to come off, the flame at the outlet tube ceased to burn. The ferrous chloride gradually darkened, and after half an hour, when the reaction was completed, it had assumed a dark bluish-gray color.

Upon breaking the tube there was found a brittle, porous substance which rarely showed any crystalline structure. It was powdered in an agate mortar, then digested with hot hydrochloric acid (1 : 12) until it was not at all attracted by the magnet, and was finally dried over sulphuric acid in an atmosphere of carbon dioxide.

Analysis of the Phosphide.—Stöckmann[1] states that he always obtained too low results for phosphorus when aqua regia was used as a solvent for spiegeleisen. He also tested the gases which were given off when the sample was dissolved, by passing them through an oxidizing medium, and in each case was able to detect phosphorus in them. For this reason we first tried other solvents, but although the phosphide was quite strongly attacked by nitric acid and by hydrochloric acid, and especially by nitric acid to which potassium chlorate was gradually added in small amounts, complete solution was in no case effected even by several hours treatment.

Portions of the phosphide were then treated with aqua regia in a small flask to which a return-flow condenser was attached.

[1] *Ztschr. anal. Chem.*, 16, 175.

After passing through the condenser the escaping gases were passed through a Mitscherlich bulb containing a solution of potassium hydroxide which had previously been saturated by chlorine. After the phosphide had been completely dissolved, the potassium hydroxide solution was acidified with nitric acid and was repeatedly evaporated with nitric acid until all chlorine had been expelled. Ammonium molybdate was then added, but no trace of a precipitate resulted. Aqua regia was, therefore, adopted as the solvent for the phosphide.

The following method of analysis was first tried:

About 0.1 gram of the phosphide was dissolved in aqua regia (one part of nitric acid to three parts of hydrochloric acid), and the solution, after being diluted, was precipitated by ammonium hydroxide. An excess of ammonium sulphide was then added to break down the ferric phosphate, and the solution was kept at 70° C. for fifteen hours. The ferrous sulphide was then filtered off, dissolved in dilute hydrochloric acid, and the iron then oxidized by bromine water. Upon precipitating this solution with ammonium hydroxide and weighing the iron as ferric oxide, too high results were obtained since the precipitate was found to contain phosphoric acid.

The method finally adopted for the analysis of the phosphide was as follows:

The sample was dissolved in aqua regia, the solution repeatedly evaporated with nitric acid, and the phosphoric acid determined by the molybdate-magnesia method. To determine the iron in the filtrate from the ammonium phosphomolybdate precipitate, the method of W. H. Krug[1] was used with satisfactory results. The iron was precipitated in the cold with ammonium hydroxide, and the ferric hydroxide, after thorough washing, was dissolved in nitric acid and again precipitated from the cold solution with ammonium hydroxide. After washing until all chlorides had been removed, the iron was weighed as Fe_2O_3.

The results obtained were as follows:

	Found.	Calculated for Fe_3P_4	Calculated for FeP
Fe	64.21	57.52	64.36
P	35.62	42.48	35.64

[1] *J. Anal. Appl. Chem.*, 5, 674.

The work of other investigators in this field had led us to expect as a product, not FeP but Fe_2P_4. Yet the constancy of composition shown by separately prepared portions of our product, its completely non-magnetic character and the agreement of the analysis with the calculated percentages, leave but little doubt as to the purity and identity of the phosphide.

The fact that the true phosphides of iron are *non-magnetic* seems to have been overlooked by recent writers, a circumstance which has probably led Hvoslef, Schneider, Percy, and others, to regard a mixture of phosphide of iron and iron (they give it the formula Fe_3P) as a definite phosphide. Howe[1] cites the work of Hvoslef and Percy, and says: "These facts suggest that iron and phosphorus preferentially combine in this particular ratio." But he does not mention the careful and extended researches of Freese upon this subject, who says:[2] "Endlich habe ich versucht, das von Hvoslef beschriebene Phosphoreisen Fe_3P, welches derselbe durch Glühen des Phosphorets FeP unter einer Decke von Borax erhalten haben will, darzustellen, allein bis jetzt vergeblich." After describing some of his own experiments, made according to Hvoslef's method, Freese concludes: "Hieraus schliesse ich, dass Hvoslef's Phosphoreisen nur ein Gemenge von Eisen mit Phosphoreisen ist, denn stets fand ich bei einem anerkannt reinen Eisenphosphoret den nach längerer Behandlung mit heisser Chlorwasserstoff saüre verbliebenen Rückstand mit dem Phosphoret gleich zusammengesetzt."

Ferric Pyrophosphate.—This salt was chosen as representing perhaps more nearly than any other the condition of the oxidized phosphorus in iron and steel. A sample of the pure ferric pyrophosphate was heated for half an hour over the full Bunsen flame: it retained its yellow color and was completely soluble in concentrated hydrochloric acid.

Experiments with Solvents.—Before attempting to separate the phosphide of iron from the pyrophosphate in samples of iron or steel, it was necessary to find a solvent which would completely dissolve the pyrophosphate and leave the phosphide unattacked. The reagents tried were solutions of ammonium oxalate, potassium oxalate, ammonium citrate, ammonium carbonate, ammo-

1 Metallurgy of Steel, p. 55.
2 *Pogg. Ann.*, **132**, 262.

nium cupric chloride, and dilute solutions of chromic, sulphuric, nitric, and hydrochloric acids; both rapid boiling and long digestion at 100° C. were employed. Clear solutions of the pyrophosphate were obtained only with ammonium oxalate, ammonium citrate, and hydrochloric acid. Portions of fifty milligrams of the pyrophosphate were then digested on a hot plate with 100 cc. of each of these three solvents. Complete solution resulted

with hydrochloric acid (1 : 1)..... in 2 minutes
" ammonium oxalate (concentrated).. " 45 "
" " citrate (sp. gr. 1.09) .... " 90 "

On diluting the ammonium oxalate solution with water a white precipitate resulted, and as this could be dissolved only by adding hydrochloric acid and boiling, the use of ammonium oxalate was abandoned.

One hundred milligram portions of the phosphide were then treated with hydrochloric acid and ammonium citrate under the same conditions as were required for the complete solution of the pyrophosphate. The residues were collected on counterpoised filters, dried, and weighed. It was found that the phosphide which had been digested with hydrochloric acid had lost about four per cent. of its weight. The filtrate from this portion, after the hydrochloric acid had been expelled by evaporation with nitric acid, gave strong tests for both iron and phosphorus. The sample of phosphide which had been digested with ammonium citrate showed no appreciable loss of weight, and hence a solution of this reagent, of a sp. gr. of 1.09, was used in the following experiments upon the separation of the pyrophosphate of iron, and phosphide of iron, in samples of iron and steel.

Before trying the ammonium citrate solution a preliminary experiment was made to ascertain the nature of the action of hydrochloric acid (1 : 1) upon the phosphorus in iron. A sample of pig iron, containing 0.205 per cent. total phosphorus, was treated with the acid until all action had ceased. The solution was filtered, the filtrate evaporated with nitric acid, and the phosphorus determined by the molybdate-magnesia method. Two determinations gave 0.153 and 0.154 per cent. phosphorus. The determination of the phosphorus in the unattacked residue showed that only 0.008 per cent. remained behind, from which

it follows that over twenty per cent. of the phosphorus present escaped in gaseous form during the solution of the iron.

The ammonium citrate separation was then tried on two samples of steel to ascertain whether the method would give agreeing results. The sample should be as finely divided as possible, and for this reason filings were used in the following determinations:

Five grams of "Open Hearth" steel was digested on a hot plate (100°), with ammonium citrate solution, for an hour and a half. The solution was then filtered through asbestos. The residue was thoroughly washed with water, dissolved in nitric acid (1.20 sp. gr.), and the phosphorus determined by the molybdate-magnesia method.

Total phosphorus in the sample was 0.044 per cent.

Phosphorus in the residue after treatment with ammonium citrate, 0.033 and 0.032 per cent.

A sample of Bessemer steel, containing 0.107 per cent. total phosphorus, gave by the same method 0.046 and 0.053 per cent. of phosphorus in the residue.

No further analyses of iron or steel samples were made, for our object in taking up the work was not the investigation of the condition of phosphorus in samples of commercial products, but was merely to attempt to devise a method to separate phosphide of iron from pyrophosphate.

The chlorine method employed by Cheever was also tried on the phosphide and pyrophosphate.

Eighty milligrams of the phosphide were heated in a current of dry chlorine. As the temperature rose sparks shot out from the surface of the phosphide. At a low red heat a glow ran through the substance which then melted and volatilized completely in a few minutes.

A sample of the ferric pyrophosphate was then heated for half an hour in a current of chlorine at the highest temperature obtainable by the use of a combustion furnace, but no loss in weight resulted.

A mixture of 0.0435 gram of the pyrophosphate, with 0.0292 gram of the phosphide, was then heated in chlorine in the same manner. The residue in the boat weighed only 0.0231 gram. As this seemed to indicate that in the volatilization the phos-

phide exerts some reducing action on the pyrophosphate, causing a volatilization of some of the constituents of the latter compound, another experiment was tried with a mixture containing a slightly higher per cent. of phosphide, to see whether there would be a correspondingly greater loss in the pyrophosphate.

0.0561 gram of the pyrophosphate, and 0.0472 gram of the phosphide, treated with chlorine, gave a residue weighing 0.0193 gram, a result which seems to sustain the above supposition.

CORNELL UNIVERSITY,
May, 1894.

NOTES ON ALUMINUM.[1]

BY GEORGE FREDERICK ANDREWS.

THE writer of this paper has made a large number of experiments with aluminum particularly with reference to its use in jewelry etc. The facts stated are the results of some of these experiments.

Alloys containing Gold.—The alloys of gold and aluminum are interesting, though of little practical use except for decorative purposes. The alloy with six per cent. of gold is as white as pure aluminum but much more brittle. The alloy with ten per cent. of gold is harder than aluminum but does not work well, except at a high temperature. Its color is light violet-brown. The alloy with fifteen per cent. of gold is a very soft fine-grained metal. It has a slight violet tint, although nearly white. The alloy with fifty per cent. of gold has a beautiful violet color. It is very soft and spongy. The alloy with seventy-eight per cent. of gold is very brittle. The color is peculiar; it is between pink and violet. The alloy with ninety per cent. of gold has a pale violet color, while the alloy with ninety-four per cent. of gold has a color approaching pink again. Alloys containing small percentages of aluminum leave a bright violet color on the cupel, under the blowpipe.

An alloy containing fifty per cent. of gold, forty-five per cent. of copper, and five per cent. of aluminum takes the color and polish of fourteen carat gold but easily tarnishes. This alloy has also been used in electroplating, but it is not entirely satisfactory for this purpose.

Alloys containing Silver.—Alloys containing from four to eight

[1] Abstract from a paper read before the Rhode Island Section, February 15, 1894.

per cent. of silver, and from ninety-six to ninety-two per cent. of aluminum are useful for many purposes. They are harder than aluminum but not brittle. They take a very fine polish and hold it well. Their color is very near that of fine silver. These alloys are now used for the manufacture of charms, medals, metal trimmings and decorations of various kinds.

Alloys containing Nickel.—The alloy containing fifty per cent. of nickel and fifty per cent. of aluminum, has a dull gray color. It is very porous and so brittle as to be useless.

The following alloys of copper, nickel and aluminum are all very hard, fine-grained and show great strength. The alloy containing sixty-six per cent. of copper, twenty-four per cent. of nickel and ten per cent. of aluminum takes a fine polish and has the color of ten carat gold. The alloy containing fifty-five per cent. of copper, thirty-three per cent. of nickel and twelve per cent. of aluminum, has a beautiful golden-brown color. The alloy containing $72\frac{1}{2}$ per cent. of copper, $21\frac{1}{4}$ per cent. of nickel and $6\frac{1}{4}$ per cent. of aluminum closely resembles it, but the color of the latter is richer and deeper. These alloys may become very useful for decorative purposes.

Solder for Aluminum.—Notwithstanding the assertions which are still heard to the contrary, aluminum can be successfully soldered. The writer has used solder which makes a clean, perfectly firm joint, and is in every way satisfactory. It requires no "soldering fluid" and no soldering iron.

Melting of Aluminum.—In melting aluminum the temperature should be kept even and not much above the melting point of the metal. The metal should be fed into the crucible in small pieces and pushed down as fast as it becomes soft. The most serviceable flux is a little tallow, although it is not necessary to use any. A sand crucible must not be used as the aluminum readily attacks the silicon.

In alloying, the aluminum should be put into the crucible after the other metal or metals have become liquid.

Restoration of the Mat.—Aluminum can be cleaned, and its peculiar mat restored by dipping for a minute and a quarter, in a solution of three ounces of caustic potash in a quart of water, then washing thoroughly and dipping in a mixture of three parts nitric, and two parts sulphuric acid, by volume.

Caustic soda can be used with nearly as good results. The main advantage in the substitution is the lower price of caustic soda.

LABORATORY OF CORNELL AND ANDREWS.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.

BY WALTER D. FIELD.

(*Continued from Vol. 15, p. 140.*)

Received September 12, 1893.

PART II.

NITRATION OF THE FIBER.

MIXED cotton and flax fiber in the form of paper, from two to three one-thousandths of an inch thick and cut into one inch squares, is nitrated by the Celluloid Manufacturing Company, and the same paper, left in long strips, one inch wide, is used for nitration by the Zylonite Manufacturing Company, of North Adams, Mass. The Celluloid Manufacturing Company introduce the cut paper into the mixed acid by means of the arrangement shown in Fig. 1, H, which is a rapidly revolving,

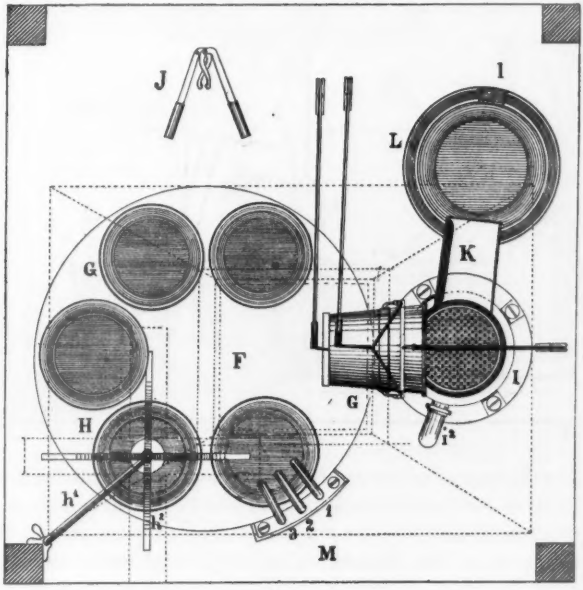


FIG. 1.

hollow tube, flared at the lower end, and immersed in the mixed acid. The centrifugal force of the revolving tube throws the paper towards the sides of the vessel G, leaving the center of the vessel ready for fresh paper. The Zylonite Manufacturing Company simply cut the paper into long strips and introduced it into the mixed acids by means of forks. The arrangement used by this company for holding the mixed acids was a cylindrical vessel divided into a number of sections, the whole revolving like a turntable, thus allowing the workman to nitrate successively each lot of paper at a given point. This company did not remove the acid from the paper after its immersion, but plunged it immediately into the water, thus losing a large proportion of acid. The Celluloid Company, on the other hand, by using the paper in smaller pieces, using more paper to a pound of acid, and wringing the mixed acid from the paper before immersion, had by much, the best process of nitration. Their method of separating the acid and paper will be seen in Figs. 1 and 2, G and I.

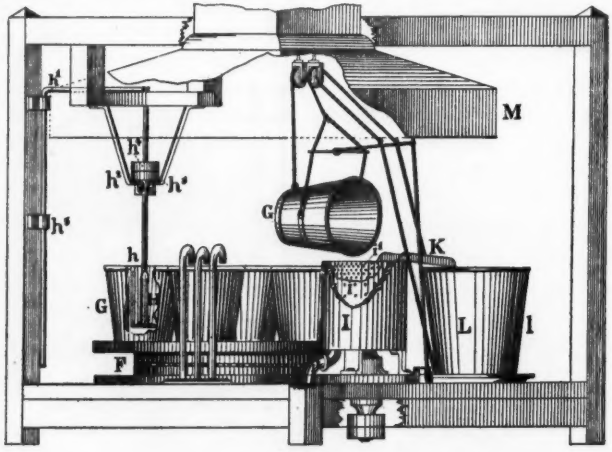


FIG. 2.

The other manufacturers of pyroxylin use earthenware vessels and glass or steel rods, hooked at one end, having small pieces of rubber hose pulled over the other end to prevent the hand from slipping. The form of vessel in general use is that given

in Fig. 3. It is sufficient in size to nitrate one pound of cotton.

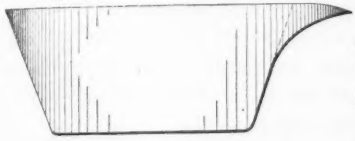
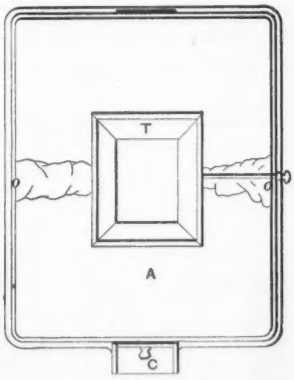


FIG. 3.

The hook on one end of the rod enables the workmen to pull the pyroxylin apart and thus insures saturation of the fiber.

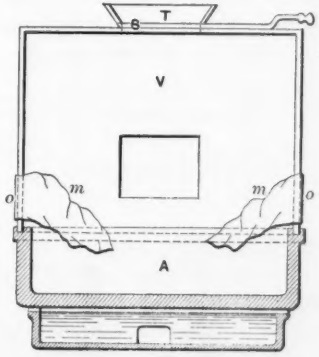
The nitrating apparatus of Tribouillet and de Besaucele (Eng. Pat., No. 5,057, 1878; Ger. Pat., No. 6,828, 1879) is given by both Bockman (Das Celluloid, 1888) and Heinzerling (Die Fabrikation Kautschuk and Guttapercha Waaren, 1883), and it is the only apparatus they mention, although Hyatt's apparatus was then in use. The plans for this nitrating box have been reproduced in Figs. 4 and 5. It is of a very unhandy construction and any workman using it would soon discard the hood V as unnecessary. The rubber sleeves would only be in his way and the acid would rot them out in a very short time.

FIG. 4.



PLAN.

FIG. 5.



SECTION.

In working by hand, at the present time, it is customary to protect the workmen from the fumes of the acid by means of a hood which is being constantly exhausted by a powerful fan or blower. They are furnished with gauntlet gloves made of white rubber, and also aprons of the same material. In the winter season the room in which the nitrating is done must be kept at a tem-

perature of about 70° F., in order to secure equality in the batches.

The nitrating apparatus of White and Schupphous (U. S. P., No. 418,237, 1889) is both novel and excellent in its general plan. The cage B (Fig. 6), with its central perforated cylinder B′ (Fig. 7), is intended to insure the rapid and perfect saturation of the tissue paper used for nitrating. The patentees say that no stirring is required with their apparatus. This might be true when paper is used, or even cotton, when the temperature of nitration is from 30° to 35° C., but would not be true if the temperature were raised to 50° or 55° C. In carrying out their process they proceed as follows: The paper is nitrated in the cage B, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder B′. After nitration the cage is carried to the wringer E, Fig. 8, of which it forms the basket, and the acids removed. Finally the cage is taken to the plunge tank F where the paper is removed from the cage by simply pulling out the central perforated cylinder B′. Fig. 9, shows the nitrating pot with its automatic cover. The plunge tank F is shown in section and plan in Fig. 10. This appara-

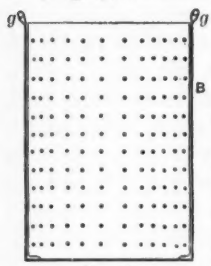


FIG. 6.

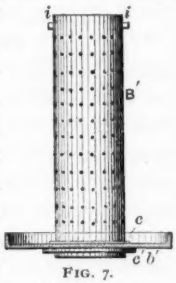


FIG. 7.

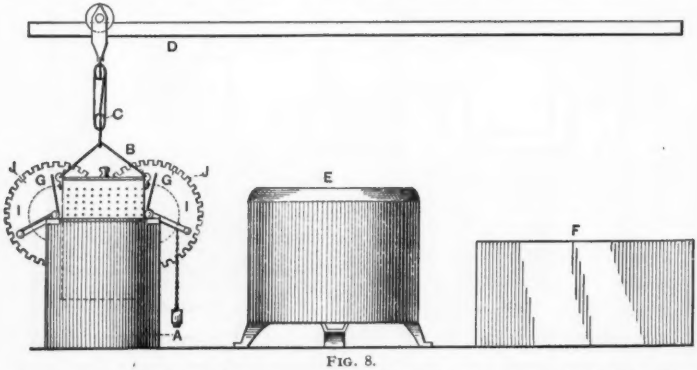


FIG. 8.

tus is given in detail because it is the only patented method that seems to be suitable for the nitration of cotton fiber in bulk at high or low temperatures.

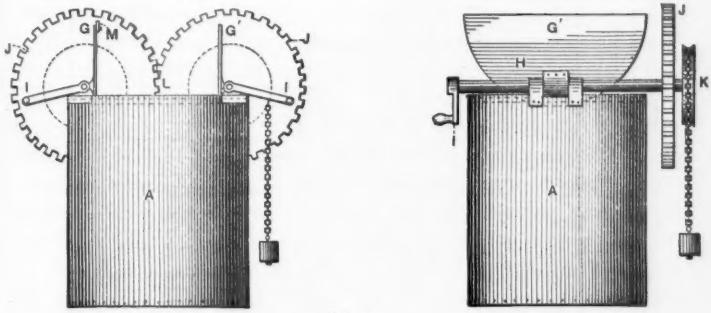


FIG. 9.

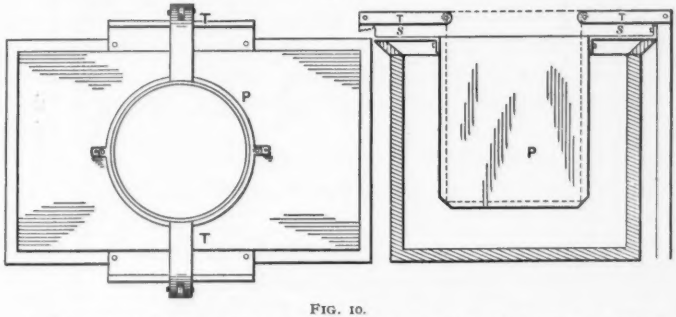


FIG. 10.

We now come to what is probably the most elaborate method of nitrating yet suggested—that is, the method patented by Mowbray, August 12, 1890 (U. S. P., No. 434,287), by which he proposes to nitrate paper in continuous lengths. The method is as yet untried. The paper loops shown in the sectional drawing (Fig. 11) are merely theoretical, for the paper web would not maintain any such position, but would settle down in the bottom of the acid tank. He allows the paper web to remain in the nitrating, or acid tank (15), from twelve to twenty minutes, then as the first part of the paper web is drawn forward, a fresh portion takes its place. One of the great problems in such an operation is how to maintain the strength of acid required in the nitrating

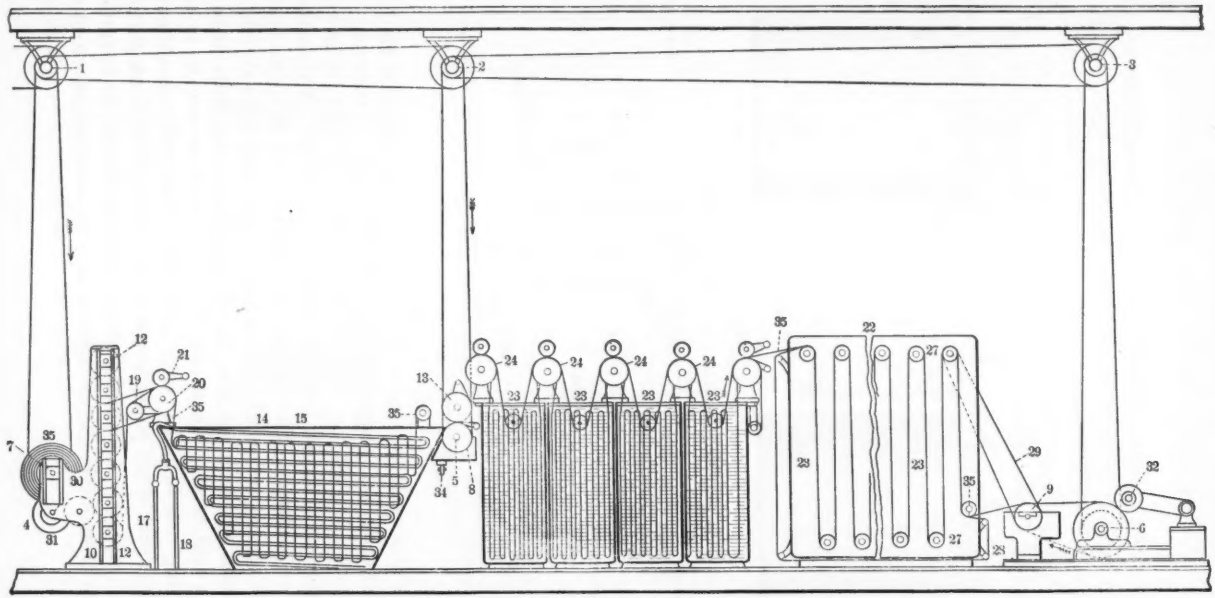

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FIG. II.

tank. Mowbray claims to be able to do this by using the methods described by him in U. S. P., Nos. 350,497, and 350,498. Such a method as Mowbray describes is certainly no better than that of Hyatt (210,611).

The best material from which to construct the various tanks required for storing the acids for nitrating vessels and for other things is, undoubtedly, steel. Mowbray, in his patent No. 350,489, 1886, claims "the use of homogeneous metal, otherwise called 'Bessemer steel' plates, for tanks, to serve as containing vessels for the mixed acids used in the process of converting cellulose into nitrocellulose." He also claims "the use of steeled cast-iron pots for holding the mixed acids, in which the cellulose is immersed during the process of conversion." Mowbray says, in the same patent: "I have discovered that cast-iron vessels treated so as to diminish the carbon therein (by exposure to continued heating, surrounded by infusoria, or iron peroxide), can be successfully used for this purpose, and that the action of acids upon metals forms a ferric sulphate which, being insoluble in the mixed nitric and sulphuric acid used, does not injuriously affect the product."

One way of constructing the vessel for holding the waste acids from the nitrating pots can be seen in Fig. 12. The inside vessel, A, is of earthenware, and may have a capacity of from 100 to 500 gallons, according to necessity. The outside vessel is of boiler steel with a flanged top, E, F. The pipe D is connected with the compressed air, and the pipe C conducts the acid as it is forced out to the desired place. It is a construction that prevents any accidents when moving the acids from place to place.

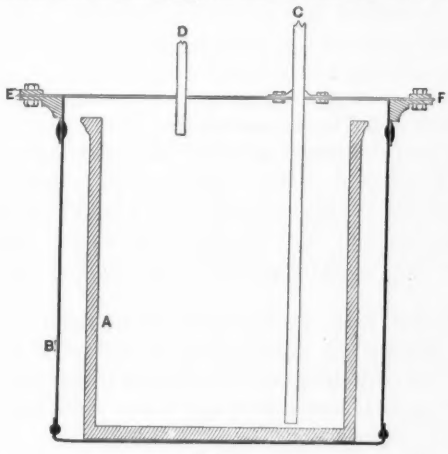

FIG. 12.

Hyatt, in U. S. P., No. 299,388, a patent for a combination of tanks so arranged as to allow of the convenient handling of the mixed acids, simply says in regard to the construction of the tanks: "We prefer to construct our tanks of wrought iron, and protect them from the corrosive action of the acids by acid-proof coatings." Steel drums will hold the mixed acids so long as they are closed from the air, but if air is allowed to enter, the sulphuric acid in the mixed acids takes up the moisture in the air, are reduced in strength at the surface, and soon begin to eat the iron or steel away. There is some choice, perhaps, in the steel to be used for such a purpose, but wrought iron is as good as steel if the air is carefully excluded from the tank. All the plants and arrangements of tanks, etc., both for nitrating and storing and using the waste acids, have been designed for an acid mixture having about the following strength:

Sulphuric acid	66 parts (absolute).
Nitric acid	17 " "
Water	17 "

the acids being used at a temperature of 30° C.

The arrangement of the plant, as described by Mowbray in U. S. P., No. 350,496, or the arrangement described in U. S. P., No. 299,388, by Hyatt, Pool, Everding, Stevens, and Wood, could not be used were the acid mixture in use of the following composition:

Sulphuric acid	62 parts (absolute).
Nitric acid	24 " "
Water	14 "

and using a temperature of 60° C. for immersion.

The nitrating apparatus of Schupphous, Mowbray, and Hyatt, were all designed for use with tissue paper as the cellulose material. The design of Schupphous might be used for cotton at low temperatures, but would be inconvenient on account of the length of time (five or six hours) required for nitrating at low temperatures.

Thus it is apparent that both the cellulose material and the method of nitrating control the construction of the nitrating plant. No plant has yet been designed for nitrating cotton fiber in its natural form at high temperatures, and using more than one pound of cotton at an immersion.

The Acid Mixture.—Many formulas have been published for producing soluble nitrocellulose. Few of them give detail enough to make them available for practical working. In many instances, although the observations were correct for the single experiment, a dozen experiments would have produced a dozen different products. Some formulas give no temperature for the immersion, others neglect even to give any specific gravities for the acids, and rather than attempt to utilize any published formula, it would be much better to spend months working out a new one to one's own satisfaction and instruction.

In the last five years, the manufacture of a pyroxylin that is almost the equivalent of the collodion cotton, has enormously increased, by reason of its use in the manufacture of pyroxylin varnishes and transparent films for photographic plates.

At the present time not more than three different formulas are in use by the manufacturers of soluble nitrocellulose in this country. The one used by the celluloid manufacturers, another in which the cotton is nitrated at high temperatures, and a third in which the temperature of the immersion is low and the time of the nitration about six hours. Of the three, the best method is the last one, or the one in which the cotton is immersed at a low temperature and then the reaction allowed to proceed in pots holding from five to ten pounds of cotton.

The following formula is essentially the one in use by the celluloid manufacturers for the production of the low form of nitrated product which they use:

Sulphuric acid	66 parts by weight.
Nitric acid	17 " " "
Water	17 " " "

Temperature of the acids at the immersion, 30° C., and the time of the immersion from twenty to thirty minutes. Cellulose in the form of tissue paper about two one-thousandths of an inch thick, one pound to 100 of acid mixture.

The nitrocellulose produced by this formula is very insoluble in the compound ethers and other solvents of pyroxylin, and is seemingly only converted or gelatinized by the action of the solvent.

The next formula produces a mixture of tetra- and penta-nitrocelluloses, hardly soluble in methyl alcohol (free from

acetone), but very soluble in anhydrous compound ethers, ketones, and aldehydes.

Nitric acid, sp. gr., 1.435	8 pounds.
Sulphuric acid, sp. gr., 1.83	$15\frac{3}{4}$ "

Cotton, fourteen ounces, temperature of immersion, 60° C. Time of the immersion, about forty-five minutes. The 60° of temperature is developed by mixing the acids together. The cotton is allowed to remain in the acid until it feels "short" to the rod.

We have here the temperature record for a single batch, (made in the form of bowl given in Fig. 1) during the time of the nitration. From four to five minutes were required to immerse the fourteen ounces of cotton and then the acids had risen in temperature from 60° to 65° C. In ten minutes the temperature in the upper part of the bowl was $63\frac{1}{2}$° C., and in the bottom 66° C. The batch was then turned over in the bowl and in another ten minutes the temperature of the top of the cotton was 59° C., and in the bottom 62° C.

At the end of thirty minutes the temperature of the top was still 59° C., and the bottom 60° C. During the remaining hour and ten minutes the temperature of the top of the acid ranged from 53° to 56° C., and from 64° to 67° C. in the bottom. The time of the immersion was one hour and forty minutes. The pyroxylin produced in this immersion was not a very soluble one, quite a large proportion being insoluble in compound ethers. It will be noticed that there were two periods in which the temperature in the batch rose, and two distinct reactions took place. If the temperature during the first thirty minutes has gone up to 70° C., or 4° higher than it did go, the cotton would have been finished inside of forty-five minutes, and the pyroxylin produced would have been perfectly soluble in compound anhydrous ethers. These observations have been verified a large number of times.

The table given below is a careful record which plainly shows the great variation in the time of the immersion and the temperature by seemingly very slight causes. The table extends over fourteen working days, during which time it rained four days. The formula used is that last given, except that the

specific gravity of the nitric acid is somewhat lower. The pyroxylin produced differs only from that produced by using a nitric acid of sp. gr. 1.43, in being soluble in methyl alcohol. From thirty to thirty-five pounds of pyroxylin were produced in each of the fourteen days.

Weather.	Specific gravity.		Time.				Temperature, degrees C.		Percentage.	
	Sulphuric.	Nitric.	Hours.	Minutes.	Hours.	Minutes.	From.	To.	Increase	Loss.
1. Clear	1.8380	1.4249	..	20	4	..	57°	62°	31	..
2. "	1.837	1.4249	..	20	2	..	60°	62°	18	..
3. Cloudy	1.837	1.4226	..	45	2	..	60°	62°	7	..
4. Rain	1.837	1.4200	..	20	1	20	60°	63°	0	0
5. Clear	1.8377	1.42	1	15	2	..	58°	62°	15	..
6 Rainy	1.8391	1.422	..	35	1	40	58°	62°	..	2
7. Cloudy	1.835	1.4226	..	20	..	35	62°	64°	..	10
8. Clear	1.835	1.4222	..	35	1	10	60°	62°	5	..
9. Partly clear	1.824	1.4271	..	20	1	..	50°	60°	..	3
10. " "	1.83	1.4271	..	10	..	25	58°	60°	..	10
11. Cloudy	1.832	1.425	..	10	..	50	58°	60°	8	..
12. Rainy	1.822	1.425	..	10	..	20	58°	60°	..	10
13. Partly clear	1.8378	1.4257	..	50	1	40	50°	58°	20	..
14. Cloudy	1.837	1.4257	1	56	4	40	50°	60°	16	..

A careful examination of this table will prove very instructive. The increase in yield varies from thirty-one per cent. to nothing, and the loss runs as high as ten per cent., yet it would be unjust to say that care was not taken to make the product uniform in quality.

On the days it rained there was a loss, with the exception of the fourth day when there was neither a loss nor a gain. On the days it was partly clear, as just before or after a rain, the table shows a loss in product. We can explain this fact by reason of the moisture-absorbing qualities of the cotton. On the rainy days it would absorb the moisture from the air until, when immersed in the acids, they were weakened, and the fiber dissolved more or less in the weakened acid, producing what is known as "burning" in the batch. It will also be noticed that on the days which show a loss, the time of the immersion was correspondingly short, as on the tenth, twelfth, and seventh days.

The lesson this table teaches is, that it is almost impossible to nitrate cellulose in small quantity and get uniform results when the nitration is carried on at high temperatures.

In the next table we have the condensed results from a month's work with the above formula.

Cotton (scoured, upland)	416 pounds,	12 ounces
Nitric acid, sp. gr. 1.42–1.425 water white	4,957 "	
Sulphuric acid, sp. gr. 1.83–1.837	9,803 "	
Product	513 "	6 ounces

The high temperature nitrating formula taken as the example in this article will be found to lead to a correct judgment of the working of all such formulas. The consideration of the cold nitration method I shall make the subject of a separate paper at some later date.

IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

By Peter S. Gilchrist.

Received May 14, 1894.

IN the JOURNAL for November, 1893, I gave a brief outline of the Hacker and Gilchrist pipe columns for saving chamber space, quoting results which had then been obtained in actual working. I wish to follow this with results of much greater interest.

As stated previously, the pipe columns were added to a plant having large chambers, the first three being each 160 feet long, and consequently not so effective as in combination with short chambers, the best work being seventeen cubic feet of chamber space per one pound of sulphur per twenty-four hours, and this with Glover and Gay-Lussac towers. The ratio of chambers have an important bearing on the amount of work done in a given space.

It has long been thought that short chambers were essential to good work, repeated experiments in Europe having demonstrated this, but there has been much tardiness in adopting them.

An observer of the chamber process notices that as the gases pass from one chamber to another a greater reaction sets in, consequently followed by an increased production of sulphuric acid. The reasons for this are obvious; the vapors strike against the surfaces of the chamber ends and the sides of the connection, causing the particles forming to interact more quickly. Again,

the gases being passed through a small aperture become better mixed, and the gases are also cooled by radiation from the lead surfaces, which is an important point in manufacturing. It has been proved in chambers of 100 feet and over, that after the gases have traversed fifty to fifty-five feet of the length the acid produced falls off considerably, so by cutting off the chamber at this point we get the maximum work from the chamber.

The important point in constructing a sulphuric acid plant is to endeavor to attain these conditions throughout the process as much as is possible, and if the mere passage of the gases from one chamber to another have such visible effects, how much more so, when these conditions are very greatly improved on, as is the case when using pipe columns.

The large, moist surfaces presented by the numerous pipes upon which the gases impinge, the thorough mixing which the gases receive by coming in contact with each successive layer of pipes, and lastly, the heat generated by the reaction, consequent upon the mixing, being carried off by the cold air passing through the pipes, are conducive to a very rapid formation of sulphuric acid.

The cyclone of last August having destroyed the acid chambers of the Darlington Phosphate Company, of Darlington, S. C., I was asked to superintend the rebuilding of the same.

The original plant consisted of three chambers, having a total capacity of 129,500 cubic feet, with a small coke tower in the rear, using Johnson's mechanical fines-furnaces, with no niter recovery, making at the outside eleven tons of 50° Beaumé acid per day.

The present plant consists of four small chambers, the first only fifteen feet long, its object being to catch the dust, the second sixty feet, the third fifty feet, and the fourth forty-three feet, having a total capacity of 100,800 cubic feet, with coke tower in the rear, using the same furnaces, and no niter recovery.

Between each chamber there is a pipe column averaging 3′.10″ by 3′.5″, and 13′.6″ high, between the last chamber and the coke tower, a small pipe case 3′.0″ by 1′.10″, and 6′.0″ long.

The average work for the last eighty-one days is as follows: Pyrites burned per day, 14,304 pounds, averaging 44.6 per cent.

sulphur, two-thirds being Virginian ore, and one-third Spanish, actually yielding forty-three per cent. sulphur. This is an equivalent of 6,153 pounds of sulphur, being 16.38 cubic feet of chamber space, per one pound of sulphur, per twenty-four hours, and in the cooler months was under fifteen cubic feet.

The average yield of acid for this period was fourteen tons of 50° Beaumé acid per day, or 4.552 pounds of 50° acid, per one pound of sulphur, per twenty-four hours.

As this means an increase over the total chamber area of seven-tenths of an inch, calculated as 50° acid, one can readily appreciate the amount of work done in the system.

The average temperatures of the chambers were as follows:

No. of chamber.	Front.	Back.
1	220° F.	222° F.
2	178° "	176° "
3	156° "	154° "
4	123° "	102° "

Atmospheric temperature, 73° F. Average oxygen in the escape gases, 6.6 per cent. Average acidity in the escape gases, 0.81 grains sulphuric anhydride per cubic foot.

The result of the application of the pipe columns over the original plant is as follows: Reduction in the size of the chambers, 21.84 per cent. Increase in the yield of sulphuric acid made, 28.18 per cent. equal to a total increase of 50.02 per cent.

Another plant is being completed in Savannah, Ga., having short chambers, pipe columns, Glover, and Gay-Lussac towers, which will, doubtless, confirm more fully the advantages of the pipe columns.

SECTIONS OF PIPES.

The construction of the pipe columns have been much improved, more especially in connection with the sections of the pipes used. The exteriors are made so as to enable the greatest amount of mixing to be got from a minimum surface of contact.

NOTE ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.[1]

By P. W. Shimer, Easton, Pa.

THE object of this note is to call attention very briefly to the influence of spinel on the determination of silica in blast-furnace slags. When fluxing aluminous ores with magnesian limestone, spinel is very apt to be found in the slag, especially when the slag is basic, the alumina in this case acting as an acid and combining with part of the magnesia to form magnesium aluminate. In the determination of silica in such a slag by the method of fusion with alkaline carbonate, the spinel seems to be almost wholly unattacked by the fusion and subsequent evaporation with hydrochloric acid, and is weighed with the silica at the end of the determination. In the case of one slag, the silica, before purification, was 34.25 per cent.; after purification with sulphuric and hydrofluoric acids, it was found to be 31.52 per cent. The bluish-colored residue left after the sulphuric and hydrofluoric acid treatment was found to dissolve easily in fused potassium bisulphate, and contained alumina and magnesia in the proportions necessary to form spinel. In the case of another slag, the silica, before separation of spinel, was 39.23 per cent.; after separation, 34.73 per cent.

The points it is desired to bring out are, that spinel is not decomposed by the usual alkaline carbonate fusion and, therefore, that it is never safe to omit the treatment of the silica with sulphuric and hydrofluoric acid. All the slags in which spinel was found were stony slags and, therefore, had the usual time in which to cool and crystallize. It is quite possible that, if the same samples had been chilled, the elements of the spinel would have remained in decomposable combination with the silica. However, even in the case of chilled samples, the possible presence of minute crystals of spinel should not be ignored, especially in basic slags rich in alumina and magnesia. By successive and repeated treatment of 100 grams of a powdered spinel slag with hydrochloric and hydrofluoric acids and boiling solution of

[1] Read before the Lehigh Valley Section, May 3, 1894.

sodium carbonate in a platinum dish, it was found to be possible to separate one gram of microscopic crystals of spinel quite free from all impurities.

NEW BOOKS.

"An Introduction to the Organic Compounds of Every-Day Life." By Julius T. Willard, M. Sc. 12mo. cloth, pp. IV; 203. Published by the author. Manhattan, Kansas. 1894. Price $1.75.

Every chemist in this country feels that anything which will tend to place organic chemistry where it belongs in our Colleges and Universities should be encouraged. It was doubtless this feeling which prompted the author to publish this little volume. The book is indeed what it pretends to be, a simple compilation. The arrangement is similar to Remsen and Bernthsen with a few changes which detract somewhat from their systematic and logical arrangement. It is on the whole so much condensed that, well-written as it is, the student must often find difficulty in following the thread connecting the various classes of compounds. The greater part of the book is devoted to the Aliphatic Series more especially to the carbohydrates. This group is neatly compiled but more appropriate for an elementary text of Applied Chemistry. Many of the every-day compounds are barely mentioned and some have been omitted entirely.

The Aromatic Series is too condensed to be of any scientific value to the student. About fifty pages are given to the derivatives of benzene proper, to naphthalene, anthracene, the terpenes, the alkaloids, the glucosides, the proteids and others. There are a good many simple facts stated, and it would seem that the book was perhaps written with the sole object of furnishing the student with these general facts.

It is, however, no longer enough that a text-book of either organic or even inorganic chemistry, be a simple mass of facts and experiments. The subject must be logically presented, leading up to, and proving new facts, by facts already known. At the same time, there must be enough assumed to develop the reasoning powers of the student and to make him feel that he is really doing the work himself. Remsen has struck the key-

note, in this respect in his "Introduction to the Study of the Compounds of Carbon" and it seems to me that it would be exceedingly difficult to place a better elementary text in the hands of the student. In fact, we are not in need of elementary text-books in organic as in inorganic chemistry. The student of organic chemistry begins with a fair knowledge of general and theoretical chemistry and a text like Bernthsen, Krafft or Richter properly used and supplemented by lectures would be far better than a small elementary book. What the organic student is most in need of is a good laboratory book, something the nature of Levy or Fischer. It is to be sincerely hoped now since organic chemistry is gaining ground in our Universities that it may not suffer from scores of poor text-books as inorganic chemistry has done.

UNIVERSITY OF MINNESOTA. G. B. FRANKFORTER.

A DETAILED COURSE OF QUALITATIVE ANALYSIS. BY ARTHUR A. NOYES pp. 80. Boston: A. D. Maclachlan, Agent, 214 Clarendon St. 1894. Price $1.

This small book of eighty pages aims to present a complete course in inorganic qualitative analysis, so arranged as to be easily followed by the student. The author follows Fresenius, in the main, as to the methods, but has modified them in some particulars. The book is divided into two parts; *viz.*, a clear, concise description of the procedure of the analysis, followed by a series of notes of explanation upon the process.

The main feature of the book, is these explanatory notes. In these the author has sought to instruct the student in all the precautions to be taken to insure accuracy, the possible sources of error, the defects in the processes, the conditions requiring a variation of the procedure, etc.

In one case thirteen, and in others nearly as many, separate notes of this kind are given. It takes, for example, fourteen pages of the book to explain how to deal with the elements of the iron group. While these notes are an excellent feature for students who have become familiar with the usual procedure, it is to be feared that the complexity of conditions they discuss, may confuse the beginner. The description of the procedure is, in most cases, incomplete without the notes, as the appearances

to be expected from the substance tested for are not given. One is obliged to hunt among the notes for the color or appearance of precipitates, etc.

But one test for each metal is given, as a rule, and nowhere are confirmatory tests given. The author plunges the student at once into the separations of the groups, omitting the usual preliminary tests for individual metals, except as they come in the separation. While there is some truth in his statement, that too much of this work is a waste of time, several confirmatory tests for each substance should be found in a complete course in qualitative analysis. Only the more difficult reactions are written out for the student.

There is neither index nor table of contents, which seriously impairs its usefulness for ready reference. While we have pointed out what seem to us its defects, especially for beginners, we must regard its main features as excellent, because of the full explanatory notes. Its chief claim to novelty is in this one feature.

E. H. Bartley.